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Kinetics of Catalytic Oxidation of Benzoin to Benzil by Alumina Supported Active MnO_2[1]

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Abstract—The kinetics of benzoin oxidation to benzil over MnO_2/Al_2O_3 was studied by investigation of the effect of initial concentration of reactant and product, catalyst mass and also temperature on the reaction rate. On the basis of obtained experimental data a rate law for the kinetics of reaction was proposed and then the reaction rate constants and activation energy of reaction were computed. Finally a simple reaction mechanism was proposed for the reaction. Also it has been shown that the rate controlling step of oxidation of benzoin to benzil is removal of hydrogen from the α-C-atom.

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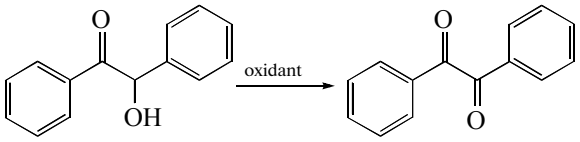
INTRODUCTION

The oxidation of alcohols to carbonyl compounds is a fundamental synthetic transformation, and a wide variety of reagents have been developed for this important reaction. Favorable attributes of an alcohol oxidation procedure include high conversions, the absence of side products, and the use of available, inexpensive, nontoxic reagents, mild condition and high chemo selectivity. The uses of solid supports in synthetic chemistry is a well established and environmentally friendly technology [1–3] and also offer a number of advantages including ease of handling, separation from the reaction product(s), selectivity and sometimes recyclability.

Heterogeneous catalytic partial oxidation of alcohols in the liquid phase is an interesting reaction for production of fine chemicals and was studied extensively up to now [4–10]. One of these reactions is the oxidation of benzoin to benzil (Scheme 1) which is one of important synthetic reactions in organic chemistry [11, 12]. Benzils are widely used for preparation of a variety of molecules [13]. This reaction has been accomplished by several reagents such as $NaBrO_3$ in CH_3CN/H_2O [14], hexadecylsilica $Cu(NO_3)_2$ in CCl_4 [15], silica $Cu(NO_3)_2$ in CCl_4 [15], MnO_2 in benzene [16, 17], $H_5PMO_{10}V_2O_{40}$ in *tert*-BuOH or THF or CH_3CN or DME [18], $Bi(NO_3) \cdot 5H_2O$–$Cu(OAC)_2$ in CH_3COOH–H_2O [11], active MnO_2/Al_2O_3 in CH_2Cl_2 [19], MnO_2/SiO_2 in CH_2Cl_2 [20], MnO_2 in viscous conditions [21], and MnO_2 or $BrMnO_4$ in solvent-free condition [22].

Manganese oxides, where the manganese can exhibit in three different valence states, are promising super capacitor materials due to the low cost of raw materials and the fact that manganese is considered environmentally friendlier than other noble metal oxides. Among the manganese oxides, MnO_2 was used to oxidize different components including pentachlorphenol [23] and 2-mercaptobenzothiazole [24].



Scheme 1.

Investigation of kinetics of reactions is important for understanding of reaction mechanism in complex systems and also reactor design. In this regards it is important to find the effect of different parameters which affect on the reaction rate, such as concentration of different species present in the solution and temperature. In spite of wide variety of reagents, which used for oxidation of benzoin to benzil, no detailed studies on the reaction kinetics and modeling have been reported.

The purpose of the present work is to investigate the reaction kinetics and modeling of oxidation of benzoin to benzil on active MnO_2/Al_2O_3 catalyst.

EXPERIMENTAL

Materials

Benzoin (99%), benzyl (99%), dicholoromethane (99%), $KMnO_4$ (99%), NaOH (99%), $MnSO_4 \cdot H_2O$ (99%), $Na_2C_2O_4$ (99%), H_2SO_4 (98%), and neutral alumina all from Merck Co. have been used for this study.

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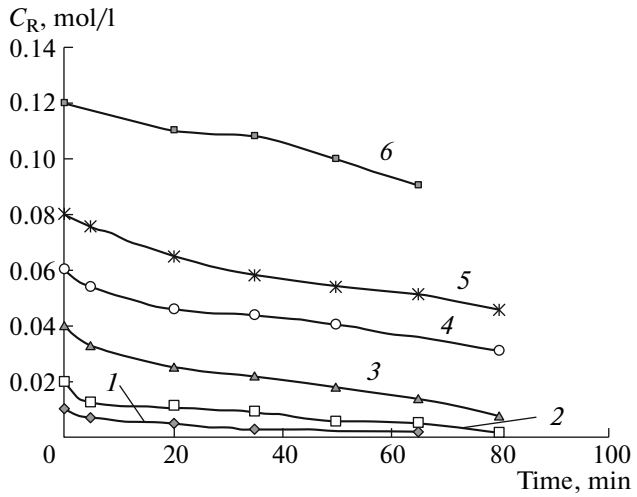


Fig. 1. Change of reactant (benzoin) concentration as a function of time at different initial concentrations of (*1*) 0.01, (*2*) 0.02, (*3*) 0.04, (*4*) 0.06, (*5*) 0.08, and (*6*) 0.12 mol/l. The concentration of catalyst is 80 g/l and the temperature is 25°C.

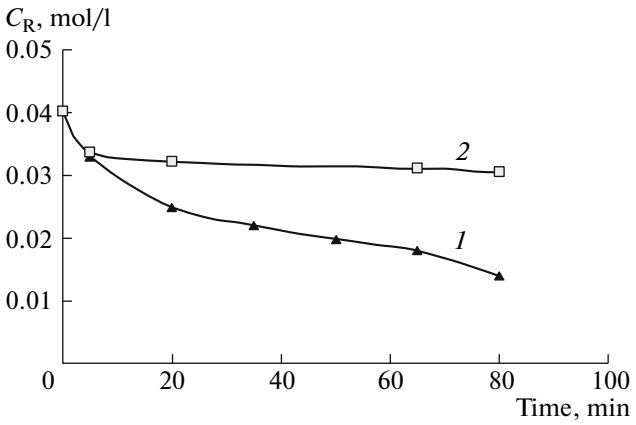


Fig. 2. Effect of absence and presence of product on the reaction rate. The initial concentration of reactant is 0.04 mol/l and temperature is 25°C. The concentration of catalyst is 80 g/l. (*1*) $C_P = 0$; (*2*) $C_P = 0.004$ mol/l.

Experimental Procedure

The active MnO_2/Al_2O_3 catalyst was prepared by the earlier method [19, 25]. Mass percent of prepared MnO_2 on Al_2O_3 was obtained according to the reported procedure [26] and was 23%.

The catalytic oxidation reaction was carried out in an agitated cell combining benzoin and alumina-supported MnO_2 in CH_2Cl_2 (as solvent) at atmospheric pressure and constant temperature, which controlled within ±0.1 K by circulating water through the jacket with a Multi Temp III thermostat.

For kinetic studies aliquot liquid samples were taken to measure concentrations of benzil at different reaction times. The concentrations of samples were measured by a spectrophotometer at 390 nm (Shimadzu model UV mini 1240V).

Effect of concentration of reactant. The oxidation of benzoin to benzil was studied with various initial concentration of benzoin (reactant), which varies between 0.01 to 0.12 mol/l. The amount of catalyst (2 g in 25 ml CH_2Cl_2) and temperature (25°C) were constant for all of these experiments.

Effect of catalyst concentration. The experiments were also carried out at different concentrations of catalyst but constant temperature (25°C) and constant initial concentration of benzoin (0.04 mol/l). Three sets of experiments were carried out with catalyst concentration of 20, 40, and 80 g/l.

Effect of temperature. The temperature effect on the oxidation of benzoin was also investigated. The reaction was carried out at temperatures 15, 20, 25, and 30°C. In these experiments the initial concentration of benzoin and catalyst were constant and 0.08 mol/l and 80 g/l respectively.

RESULTS AND DISCUSSION

The decrease of benzoin concentration (C_R) due to oxidation over MnO_2/Al_2O_3, as a function of time and at various concentrations of benzoin is shown in Fig. 1. We have tried to account for the obtained data with different rate laws. The analysis of experimental data (Fig. 1) reveals that at low concentration of reactant, the rate increases linearly with concentration but at higher concentrations the increases of rate is lower than linear one. This behavior suggests the following relation between the concentration of reactant C_R and the rate of reaction, w:

$$w \propto \frac{K_R C_R}{1 + K_R C_R}, \quad (1)$$

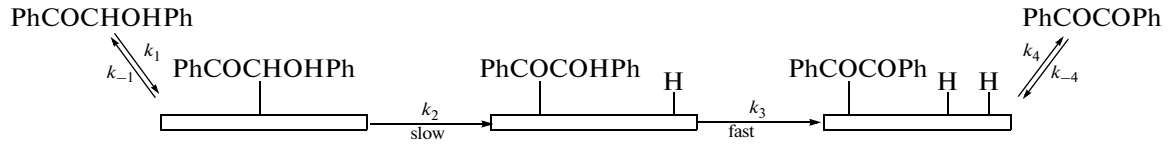
where K_R is the adsorption constant of reactant.

The variation of benzoin concentration C_R at various times in the initial presence and absence of product were plotted in Fig. 2. The experimental data (Fig. 2) shows that the rate decreases with increasing the product concentration, therefore Eq. (1) can be modified to:

$$w \propto \frac{K_R C_R}{1 + K_R C_R + K_P C_P}, \quad (2)$$

where C_P is the product concentration and K_P is the adsorption constant of product. Figure 3 shows the effect of catalyst concentration on the reaction rate. The data of this Figure reveals that by increasing the catalyst concentration the rate of reaction increases, so

$$w \propto \frac{K_R C_R}{1 + K_R C_R + K_P C_P} M_C, \quad (3)$$



Scheme 2.

where M_C is the concentration of catalyst (g/l). Finally the rate law of reaction can be written as:

$$w = \frac{-dC_R}{dt} = \frac{kK_RC_R}{1 + K_RC_R + K_PC_P} M_C, \quad (4)$$

where k is the rate constant of reaction.

The derived equation for rate law (Eq. (4)) of benzoin oxidation to benzil by MnO_2/Al_2O_3 is similar to the rate law of glucose oxidation by Pd/Al_2O_3 which was reported previously [27].

Following we will show that the derived rate law (Eq. (4)) is compatible with the experimental data of the present system. Then the constants of Eq. (4) will be calculated. On the basis of law of mass conservation one has:

$$C_P = C_0 - C_R, \quad (5)$$

where C_0 is the initial concentration of reactant and C_R is its concentration at any time. By substitution of Eq. (5) in Eq. (4) one obtains:

$$w = \frac{kK_RC_R}{1 + K_PC_0 + (K_R - K_P)C_R} M_C. \quad (6)$$

Since benzil and benzoin are nearly similar in structure and electronic factors, it can supposed that their adsorption constants are nearly the same i.e., $K_R \approx K_P$. This assumption will be justified latter. Therefore Eq. (6) reduces to Eq. (7):

$$w = \frac{kK_RC_R}{1 + K_PC_0} M_C \quad (7)$$

or

$$w = \frac{-dC_R}{dt} = k''C_R, \quad (8)$$

where

$$k'' = \frac{kK_RM_C}{1 + K_PC_0}. \quad (9)$$

Equation (8) shows that the rate law is pseudo first order with respect to the reactant but its rate constant (k'') is a function of initial concentration of reactant and also amount of catalyst. Integration of Eq. (8) leads to:

$$\ln\frac{C_R}{C_0} = -k''t. \quad (10)$$

Equation (10) reveals that if our assumption ($K_R \approx K_P$) is correct, then the plot of $\ln C_R$ vs. t should be linear with different slopes (k'') for various initial concentration of reactant. Figure 4 shows the diagram of $\ln C_R$ vs. t at different initial concentration of reactant. The linearity of these diagrams shows that our assumption

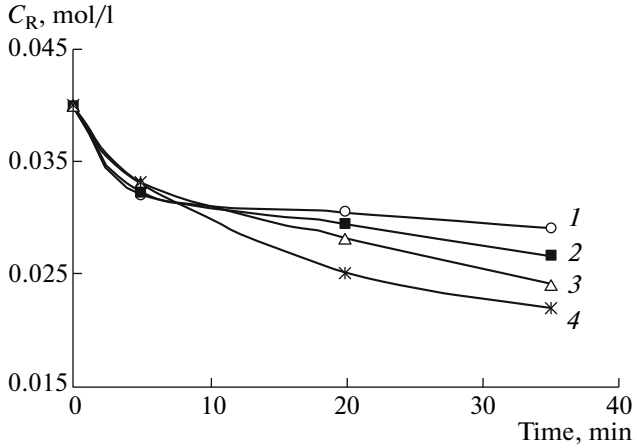


Fig. 3. Effect of catalyst concentration on the reaction rate. The initial concentration of reactant is 0.04 mol/l and temperature is 25°C. M_C = (*1*) 20, (*2*) 30, (*3*) 40, and (*4*) 80 g/l.

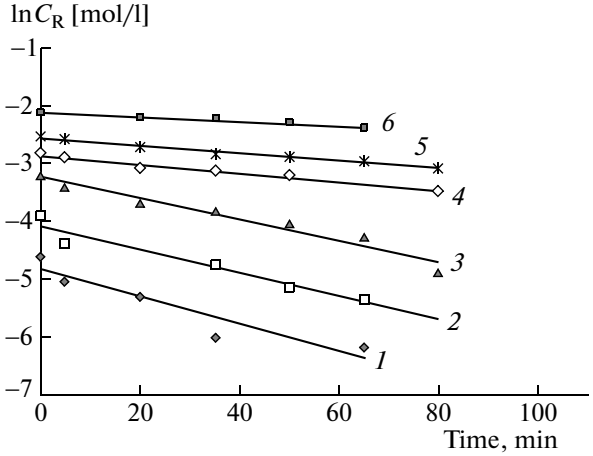


Fig. 4. Linear plot of $\ln C_R$ as a function of time at different initial concentration of reactant. C_0 = (*1*) 0.01, (*2*) 0.02, (*3*) 0.04, (*4*) 0.06, (*5*) 0.08, and (*6*) 0.12 mol/l.

($K_R \approx K_P$) and also the derived rate law are acceptable. The values of k'' computed from the slopes (Fig. 4) and listed in Table 1. From Eq. (9) one can define k' as:

$$k' = \frac{k''}{M_C} = \frac{kK_R}{1 + K_P C_0}. \quad (11)$$

Since the concentration of catalyst (M_C = 80 g/l) was constant, the values of k' were calculated simply by Eq. (11) and listed in Table 1. Rearrangement of Eq. (11) gives:

$$\frac{1}{k'} = \frac{1}{kK_R} + \frac{K_P C_0}{kK_R} \quad (12)$$

and since, $K_R \approx K_P$ so Eq. (12) reduces to:

$$\frac{1}{k'} = \frac{1}{kK_R} + \frac{C_0}{k}. \quad (13)$$

This equation shows that the plot of $1/k'$ vs. C_0 should be linear and the true rate constant (k) and adsorption constants (K_R or K_P) can be evaluated from the slope and intercept respectively. Figure 5 shows the plot of $1/k'$ vs. C_0 at 25°C. The good linearity of this plot again confirms our proposed rate law and assumptions. The obtained values for rate constant (k) and adsorption constant (K_R or K_P) at 25°C are 7×10^{-6} mol g^{-1} min^{-1} and 100 l/mol respectively.

For investigation the effect of temperature on the reaction kinetics the experiments were carried out at four different temperatures ranging from 15 to 30°C at constant catalyst concentration (M_C = 80 g/l) and constant but high reactant concentration (C_R = 0.08 mol/l). In this condition since the initial concentration of solute is high, one can assume $1 \ll K_P C_0$ in Eq. (11) and therefore arrives:

$$k' = \frac{kK_R}{K_P C_0} \quad (14)$$

Table 1. The values of pseudo rate constants, k'' and k' at various initial concentrations of reactant (C_0)

C_0, mol/l	k'', min^{-1}	k', l/(g min)
0.01	0.0238	2.98×10^{-4}
0.02	0.0200	2.50×10^{-4}
0.04	0.0116	1.45×10^{-4}
0.06	0.0076	9.50×10^{-5}
0.08	0.0068	8.50×10^{-5}
0.12	0.0042	5.25×10^{-5}

Table 2. The values of rate constants, k at various temperatures C_0 = 0.08 mol/l and M_C = 80 g/l

T, K	k, mol/(g min)
288	3.9×10^{-6}
293	5.3×10^{-6}
298	6.6×10^{-6}
303	1.0×10^{-5}

and since $K_R \approx K_P$ Eq. (14) simplifies to:

$$k' = \frac{k}{C_0} \quad (15)$$

therefore on the basis of Eqs. (10) and (15) one arrives that at high concentration of reactant the plot of the $\ln C_R$ vs. t should be a line with slope of kM_C/C_0. Figure 6 shows the plot of $\ln C_R$ vs. t at different temperatures. From the slopes of these plots the values of rate con-

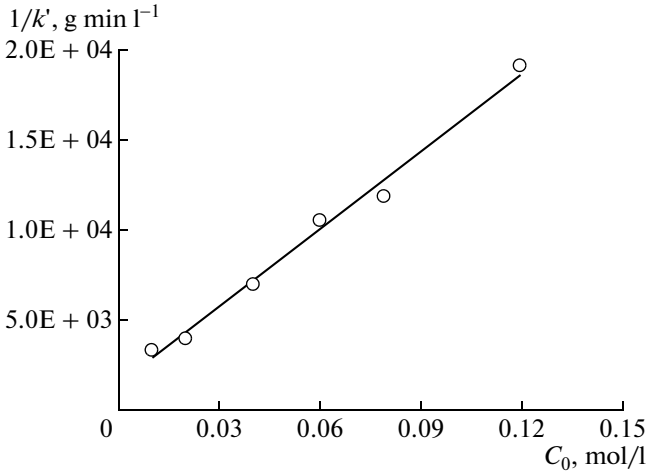


Fig. 5. Plot of inverse of $1/k'$ vs. initial concentration of reactant at 25°C.

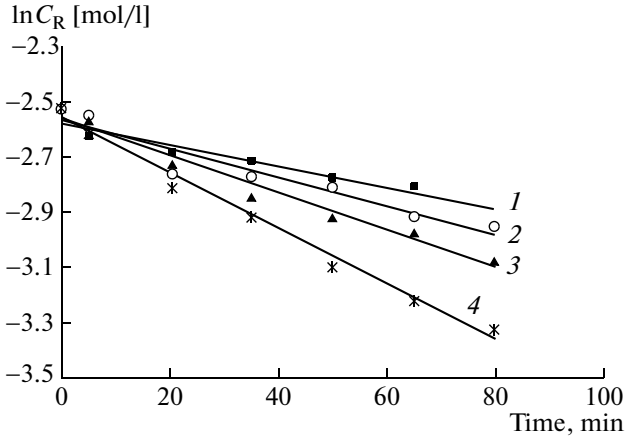


Fig. 6. Linear plot of $\ln C_R$ as a function of time at different temperatures. C_0 = 0.08 mol/l, M_C = 80 g/l. T = (*1*) 288, (*2*) 293, (*3*) 296, and (*4*) 303 K.

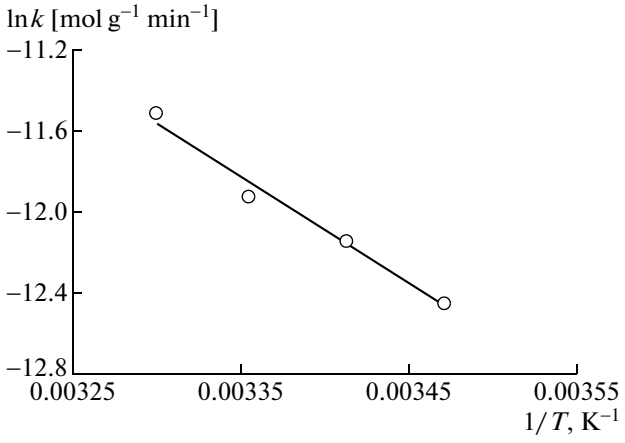


Fig. 7. Arrhenius plot of ln$k$ vs. $1/T$ for derivation of reaction activation energy.

stants were computed at different temperatures and listed in Table 2. As it shown in Table 2 by increase of temperature the value of rate constant increases. This means that the reaction is faster at highest temperatures. On the basis of Arrhenius plot (ln$k$ vs. $1/T$) it is possible to derive the activation energy of reaction. Figure 7 shows the Arrhenius plot of the present system. From the slope of this plot the activation energy for oxidation of benzoin to benzil over MnO_2/Al_2O_3 were computed and is 10.4 kcal/mol.

A proposed simple mechanism for oxidation of benzoin to benzil is presented in Scheme 2. In this proposed mechanism, benzoin adsorbs reversibly onto active site of catalyst, and then undergoes dehydrogenation from the α-C-atom by rate constant k_2. The next step is the dehydrogenation from O–H group by rate constant k_3. Finally the produced benzil desorbs from the surface by rate constant k_4 although there is a possibility for re-adsorption of product by rate constant k_{-4}. If we suppose that removal of hydrogen from α-C-atom (step 2) is the rate-controlling step as it is proposed by others [4, 6], i.e., k_2 is very small, and therefore the change in surface concentration of adsorbed benzoin is negligible, then it is possible to estimate the surface concentration of benzoin ($\theta_{RR'CHOH}$) via the competitive Langmuir isotherm (by considering that both the reactant and product can be adsorbed competitively in the same sites):

$$\theta_{RR'CHOH} = \frac{K_R C_R}{1 + K_P C_P + K_R C_R}, \quad (16)$$

where $K_R = k_1/k_{-1}$ and $K_P = k_{-4}/k_4$. Since it has been supposed that the step 2 is rate controlling step:

$$w = k_2 \theta_{RR'CHOH}. \quad (17)$$

By substitution of Eq. (16) in Eq. (17), one arrives:

$$w = \frac{k_2 K_R C_R}{1 + K_P C_P + K_R C_R}. \quad (18)$$

Equation (18) which obtained from the proposed mechanism (Scheme 2) is the same as Eq. (4) which obtained from the experimental data. So it is concluded that the proposed mechanism is an acceptable mechanism for oxidation of benzoin to benzil over MnO_2/Al_2O_3 catalyst. Also it can be concluded that the rate determining step of this reaction is removal of hydrogen from α-C-atom.

CONCLUSIONS

It was observed that the rate of oxidation of benzoin to benzil over MnO_2/Al_2O_3 increases with increase of both benzoin and catalyst concentration. Because of competitive behavior of reactant and product for adsorption on the surface of catalyst, the presence or appearance of product (benzil) has a negative effect on the rate of reaction. By increasing of temperature the rate of reaction increases. On the basis of experimental data the obtained equation (Eq. (4)) is an appropriate rate law for this system. Since the rate law of proposed mechanism is the same as Eq. (4), the Scheme 2 considered as a suitable mechanism for oxidation of benzoin to benzil over MnO_2/Al_2O_3. The rate limiting step of this catalytic reaction is removal of hydrogen from the α-C-atom.

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