Kinetics and Mechanism of Slurry Phase Air Oxidation of Benzyl Alcohol over Zirconium Vanadate Catalyst

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The kinetics of slurry phase air oxidation of benzyl alcohol to benzaldehyde over zirconium vanadate catalyst is reported in this study. Initial rates for the formation of product were determined by varying the partial pressures of the reactants. The data collected were found to satisfy a rate law: $R = [(k_1P_Bk_2P_o)/(k_1P_B + k_2P_o)]$. The study suggests that reaction follows a Mars-Van Krevelen type of redox mechanism.

Keywords: Benzyl alcohol, Zirconium vanadate, Oxidation, Kinetic study.

INTRODUCTION

Catalytic oxidation of benzyl alcohol to benzaldehyde is an important chemical reaction. The products find their use in various industries like pharmaceuticals, perfume industries, chemical industries, agriculture, *etc.* [1-5]. Oxidizing agents *viz.* pyridinium dichromate (PDC), pyridinium chlorochromate (PCC), $Na_2Cr_2O_7$, CrO_3, $KMnO_4$, *etc.* have been extensively used for carrying out liquid phase oxidation of alcohols [6-14].

Problems associated with these catalysts are their poor performance, toxic nature, difficult handling, production of hazardous substances and disposal. Peroxides are also used as oxidant along with phase transfer catalysts for the liquid phase oxidation of alcohols. The major drawbacks associated with these processes are difficulty in separation and non-reusability of the catalyst [15-18]. Molecular oxygen/air with heterogeneous catalyst provides better option to overcome these problems. Solid catalysts like supported platinum-group metals (mostly Pt and Pd), supported Ag & Au, metal oxides, mixed metal oxides, molecular sieves, hydrotalcites, phosphates and heterogenized metal complexes are widely used for the oxidation of alcohols [19-26].

Kinetics of benzyl alcohol oxidation studied over many homogeneous and heterogeneous catalysts and mechanism of the reaction has been proposed. Studies in homogeneous phase were mainly carried out over the catalysts like acid permanganate,

aqueous dichromate, fluorochromate tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB), *etc.* [27-31]. Heterogeneous phase kinetic studies were carried out mainly over supported Au, Au-Pd nanoparticles, carbon supported Pd nanoparticles and Pt nanoparticles [19,31-38].

Insight of reaction mechanism is an essential piece of information required to design efficient chemical reactors for the large scale production of various compounds. There are five steps involved in catalytic reactions: (i) diffusion of reactants to the catalyst surface *i.e.* mass transfer, (ii) adsorption of reactants on the catalyst surface, (iii) surface reaction, (iv) desorption of products from catalyst surface, and (v) diffusion of products to the bulk solution. First and fifth steps are the physical processes and require small activation energy. These steps are necessarily eliminated while investigating the reaction mechanism. First step *i.e.* diffusion of reactants can be eliminated by taking the appropriate particle size range of the catalyst in which rate is independent of it. Effect of diffusion of products is eliminated by keeping the conversion as low as possible (generally < 20%). Other factors like effect of stirring speed and catalyst concentration on the rate are also eliminated. Under these conditions reaction will be only forward and rates will be initial rates.

In the present work, nanoporous zirconium vanadate (ZrV_2O_7) catalyst was prepared by solution combustion method [39,40]. To the best of our knowledge, there is no report on the kinetics of slurry phase air oxidation of benzyl alcohol to

benzaldehyde over ZrV_2O_7 catalyst. The objectives of the present work were: (i) to collect the data on the kinetics of the process, (ii) to find the activation energy of the reaction, and (iii) to predict a suitable mechanism.

EXPERIMENTAL

Nanoporous ZrV_2O_7 catalyst was prepared by solution combustion method. AR grade (Merck) zirconium nitrate, ammonium meta vanadate and citric acid (as fuel) were used. In a typical preparation, 12.32 g of zirconium nitrate, 0.65 g of ammonium metavanadate and 25.92 g of citric acid were mixed in minimum quantity of water to make a slurry. The slurry was heated over a hot plate where it swells into a gel. The resultant product was grinded and kept in the muffle furnace for the calcination at 550 ºC for 4 h. The obtained yellow green product was further grinded in order to prepare a fine powder.

Oxidation of benzyl alcohol over ZrV_2O_7 catalyst was carried out in a three necked round bottom flask fitted with magnetic stirrer, thermometer pocket, feed unit and the condenser. The flask was heated over a hot plate (with magnetic stirrer). A manometer was used to measure the flow of air. Reactant along with solvent (dichloromethane) was fed into the reactor and air was passed through the reaction mixture. At the end of run reaction, the mixture was allowed to cool and filtered to separate the catalyst. In order to obtain the initial rates, time of run (30 min) was adjusted to ensure the minimum conversion.

Following equation was used to calculate the rates:

Rate of the formation of benzaldehyde (mol h^{-1} m^{-2}) =

$$\frac{\text{Mols of the product formed per hour}}{\text{Surface area of the catalyst}}$$

Data were collected by keeping partial pressure of oxygen (P_o) constant and varying the partial pressure benzyl alcohol (P_B). Similarly data were also collected by varying P_o and keeping P_B constant. The rate constants k_1 and k_2 were calculated by plotting the graph between 1/rate *versus* 1/P_B and 1/rate *versus* P_o, respectively. The reaction was carried out at two different temperatures to find the activation energy, which was calculated by using the Arrhenius equation:

$$\ln\frac{K_{80}}{K_{70}} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where, T_1 and T_2 are absolute temperature (T_1 = 343.15 K and T_2 = 353.15 K), K_{70} and K_{80} are rate constants at T_1 and T_2, respectively, R is Universal gas constant (R = 8.314 J/mol).

After the completion of each run, the reaction mixture (containing product) was analyzed with the help of chemito1000 Chromatograph using SE-30 column and FID detector.

RESULTS AND DISCUSSION

Effect of catalyst loading on rate: Effect of catalyst loading on the reaction rate was studied by keeping the temperature and partial pressure of the reactants constant. Data obtained by the experiments are graphically represented in Fig. 1. Results revealed that there was a constant increment in the rate till catalyst loading of 2.5% of benzyl alcohol. After that rate became almost constant.
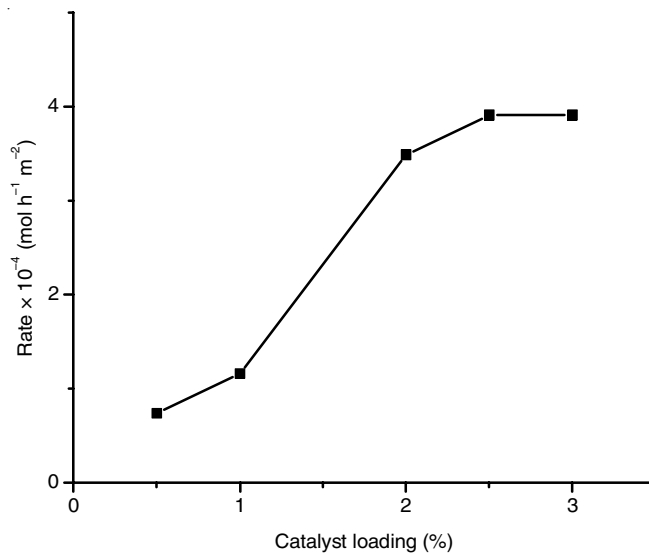

Fig. 1.	Effect of catalyst loading (%) on rate of the formation of benzaldehyde. Amount of benzyl alcohol = 5 mL, temperature = 80 ºC, time of run = 0.5 h, air flow rate = 30 L h^{-1}

Effect of stirring speed on rate: Effect of stirring speed on the conversion rate of benzyl alcohol oxidation was studied over ZrV_2O_7 catalyst by keeping all other variables constant (Fig. 2). Experimental results indicate that the rate of conversion of benzyl alcohol increases with increase in stirring speed and reaches to the maximum at 750 rpm. After that no effect of stirring speed on conversion rate was observed.
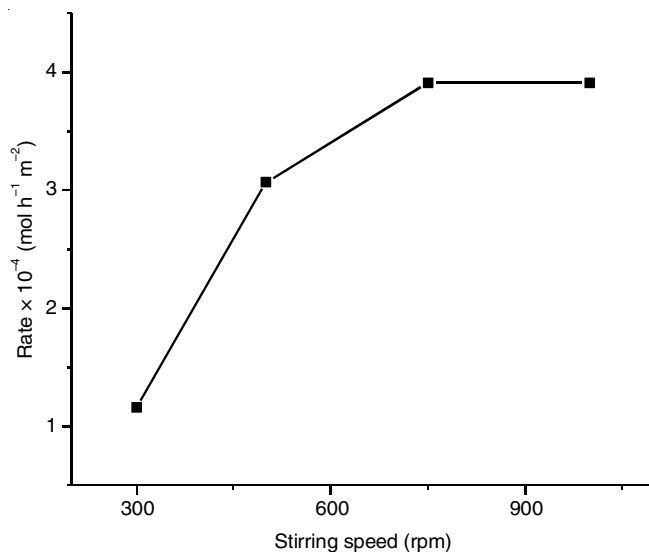

Fig. 2.	Effect of stirring speed on rate of the formation of benzaldehyde. Amount of benzyl alcohol = 5 mL, temperature = 80 ºC, time of run = 0.5 h, catalyst concentration = 2.5%, air flow rate = 30 L h^{-1}

Effect of partial pressure of benzyl alcohol on rate: Effect of partial pressure of benzyl alcohol on initial rate was studied at constant partial pressure of oxygen and at constant temperature (Fig. 3). The rate varied almost linearly at low partial pressure and became constant at higher partial pressure.

Effect of partial pressure of oxygen: Effect of partial pressure of oxygen on initial rate was studied at constant temperature and at constant partial pressure of benzyl alcohol. Rate
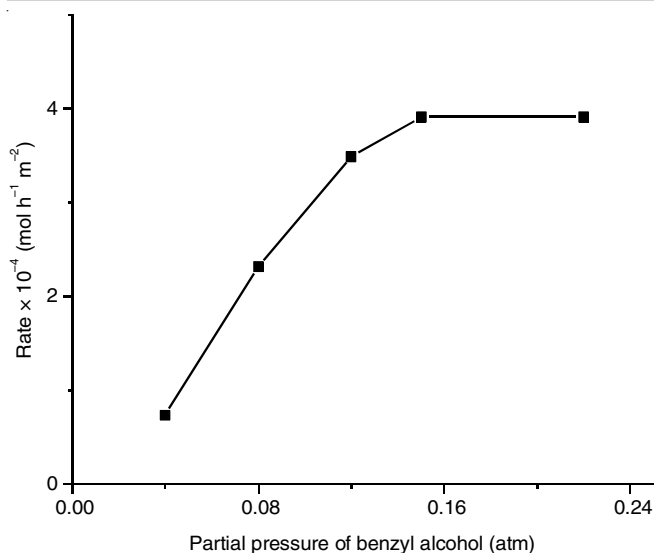
Fig. 3. Effect of partial pressure of benzyl alcohol. Temperature = 80 ºC, Time of run = 0.5 h, catalyst concentration = 2.5%, air flow rate = 30 L h^{-1}
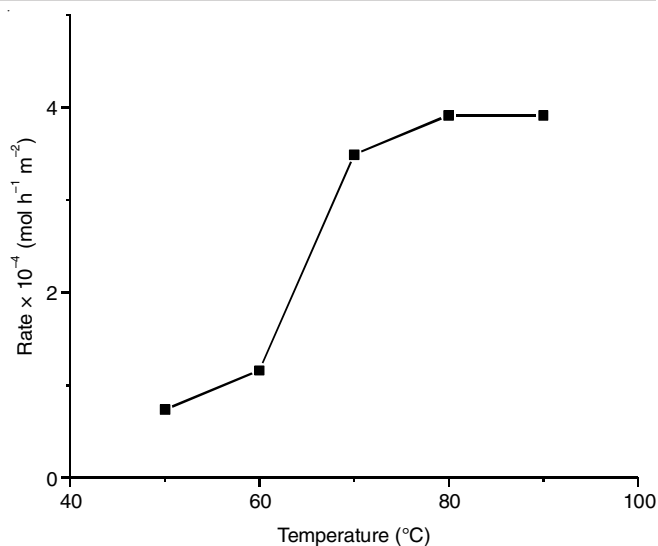
was observed to increase in the beginning and became almost constant at higher partial pressure of oxygen (Fig. 4).
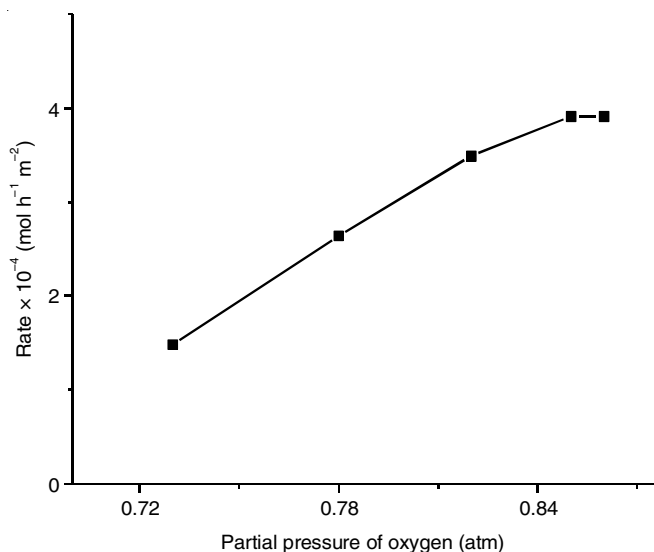

Fig. 4. Effect of partial pressure of oxygen. Amount of benzyl alcohol = 5 ml, Temperature = 80 °C, time of run = 0.5 h, catalyst concentration = 2.5%

Effect of temperature on rate: Variation of initial rate with temperature was studied at constant partial pressure of benzyl alcohol and that of oxygen (Fig. 5). It increases up to 80 °C and became constant beyond that.

Kinetic evolution: In present study, the mechanism of the reaction is proposed on the basis of a redox model given by Mars and Krevelene. Mars-Van Krevelene (MVK) mechanism is applicable to the oxidation of hydrocarbons over mixed metal oxide catalysts. According to this model, oxidation of organic compound takes place in two steps: (i) oxidation of substrate on the catalyst surface, and (ii) re-oxidation of partly reduced catalyst surface by means of oxygen. Thus equilibrium is maintained between the reduced catalyst and the oxidized catalyst

Fig. 5. Effect of temperature on rate of the formation of benzaldehyde. Amount of benzyl alcohol = 5 mL, time of run = 0.5 h, catalyst concentration = 2.5%, air flow rate = 30 L h^{-1}

and a rate equation can be derived on the basis of MVK model. If the obtained kinetic data satisfactorily follow the rate law, the mechanism proposed by model is applicable to the reaction. The initial rates were kept independent of catalyst loading and stirring speed hence mass transfer and diffusion were not rate controlling. Remaining three factors may involve in controlling the reaction steps. Thus, the rate equation based on adsorption, surface reaction and desorption of products was derived and tested for validity.

Suppose θ_{OX} is the fraction of the surface which is in the oxidized form, then $(1 - \theta_{OX})$ is the fraction of the surface which is in reduced state, then-

$$\text{Rate of reduction of catalyst} = k_1 P_B \theta_{OX} \qquad (1)$$

$$\text{Rate of oxidation of catalyst} = k_2 P_o (1 - \theta_{OX}) \qquad (2)$$

At equilibrium,

$$k_1 P_B \theta_{OX} = k_2 P_o (1 - \theta_{OX})$$

$$k_1 P_B \theta_{OX} = k_2 P_o - k_2 P_o \theta_{OX}$$

$$\theta_{OX} (k_1 P_B + k_2 P_o) = k_2 P_o \qquad (3)$$

Therefore,

$$\theta_{OX} = k_2 P_o / (k_1 P_B + k_2 P_o) \qquad (4)$$

Rate of oxidation of organic compound = $k_1 P_B \theta_{OX}$
On substituting value of θ_{OX} from eqn. 4
Rate of oxidation of organic compound

$$R = k_1 P_B k_2 P_o / (k_1 P_B + k_2 P_o)$$

or

$$1/R = (k_1 P_B + k_2 P_o) / k_1 P_B k_2 P_o$$
$$1/R = (1/k_2 P_o) + (1/k_1 P_B) \qquad (5)$$

Thus, if rate of the reaction is determined at constant partial pressure of oxygen and varying partial pressure of benzyl alcohol and 1/R is plotted against $1/P_B$ a straight line should be obtained. Its slope will be equal to $1/k_1$.

If a graph is plotted between $1/P_o$ and 1/R a straight line will be obtain. Its slope will be $1/k_2$. In present study, we collected data on rate of reaction by varying the P_o at constant

P_B and on rate of reaction by varying P_B at constant P_o. The plot of 1/R *versus* $1/P_B$ is shown in Fig. 6. The k_1 is found to be 1.62×10^{-3}. The plot between 1/R and $1/P_o$ is represented in Fig. 7 and k_2 is found to be 4.37×10^{-5}. Activation energy of the reaction was found to be 45.95 kcal mol^{-1}.
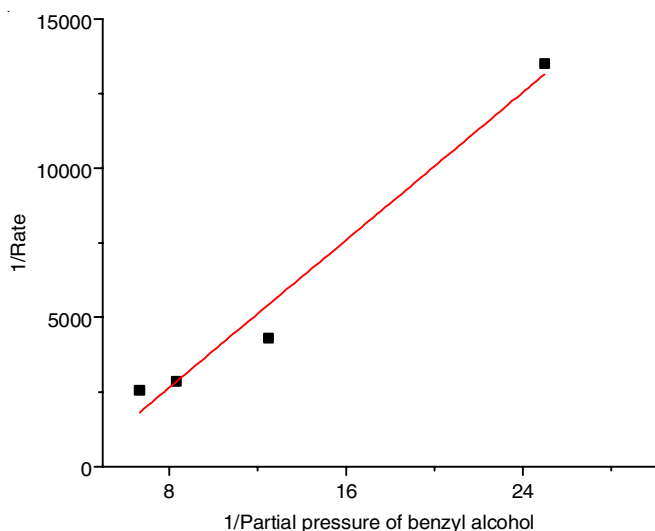

Fig. 6.　Plot between 1/R and $1/P_B$. Temperature = 80 °C, time of run = 0.5 h, catalyst concentration = 2.5%, air flow rate = 30 L h^{-1}
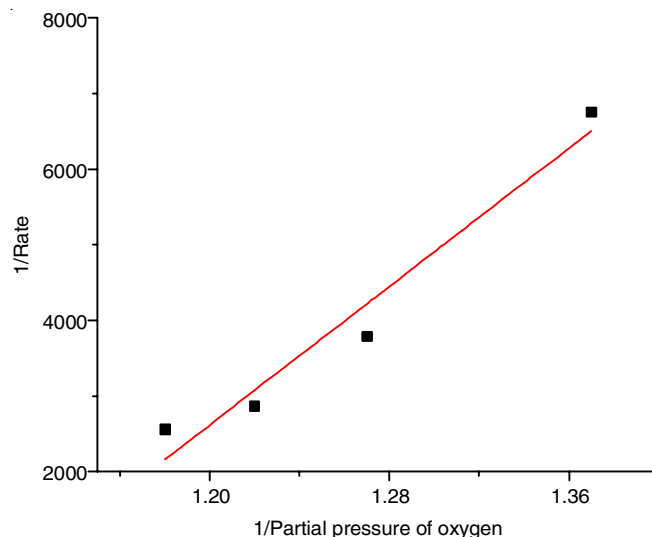

Fig. 7.　Plot between 1/R and $1/P_O$. Amount of benzyl alcohol = 5 mL, temperature = 80 °C, time of run = 0.5 h, catalyst concentration = 2.5%

Conclusion

Kinetics of slurry phase oxidation of benzyl alcohol by air over ZrV_2O_7 catalyst has been studied under initial state
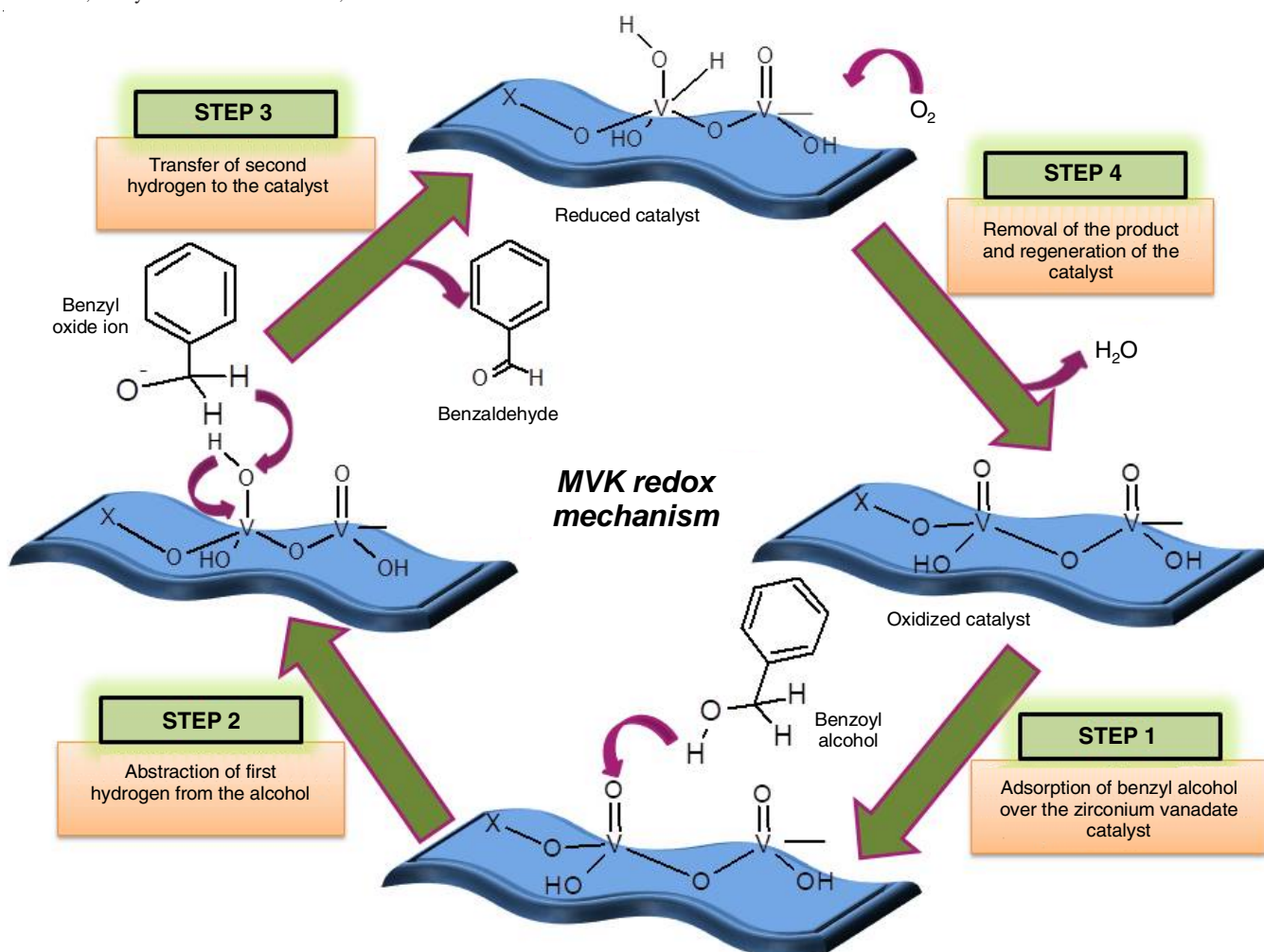

Fig. 8. Proposed mechanism: Oxidation of benzyl alcohol over ZrV_2O_7 catalyst

conditions. Data has been collected for the formation of benzaldehyde. A rate law $R = [(k_1P_Bk_2P_o)/(k_1P_B + k_2P_o)]$ has been derived on the basis of Van-Mars Krevelen model. This model assumes a study state between oxidized and reduced from of the catalyst. The observed data are found to obey this model. Based on the studies, a tentative mechanism for the reaction has been suggested in Fig. 8. The activation energy for the 'hydrogen' abstraction from the $-CH_2$ group of benzyl alcohol is found to be highest and proposed to be rate determining step.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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