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Friedel−Crafts Alkylation of Diphenyl Oxide with Benzyl Chloride over Sulphated Zirconia

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Abstract:

Friedel−Crafts reactions are ubiquitous in fine chemicals, intermediate, and petrochemical industries. In most of the cases very high yield and selectivities can be achieved with aluminium chloride as catalyst with nitrobenzene as a solvent. However, environmental concerns associated with aluminium chloride−nitrobenzene or BF_3−HF or mineral acids catalysts have encouraged process changes and the development of solid acid-based Friedel−Crafts reactions which are economically viable as well. This contribution deals with the alkylation of diphenyl oxide with benzyl chloride using sulphated zirconia as solid acid catalyst, which gives excellent conversions of the product benzyldiphenyl oxide. The effects of a variety of parameters were studied in a batch reactor to establish the kinetics and mechanism of the reaction at 90 °C. The reaction obeys the Langmuir−Hinshelwood−Hougen−Watson mechanism involving weak adsorption of the reactants, and the reaction is intrinsically kinetically controlled.

Introduction

The use of acid catalysts is very widespread in the chemical and allied industries, and the highly corrosive, hazardous, and polluting liquid acids employed by those technologies are being replaced with solid acids, for instance, acid-treated clays, zeolites, ion-exchange resins, and a variety of metal oxides. Of late, a number of organic syntheses are conducted with solid acids, leading to better regio- and stereoselectivity. Not only the strength of the acid but also the type of acidity (Brønsted or Lewis) are factors for obtaining enhanced activity and selectivity. The incorporation of superacidity in solid acids has attracted considerable attention. Among solid acids, sulphated zirconia (S-ZrO_2) has found several applications,[1−7] and we have observed that it holds great promise in a number of reactions of industrial importance,[6−16] for instance, condensation, esterification, alkylation, etherification, acylation, isomerisation, and nitration. Due to its low cost, high thermal stability, and superacidity in certain reactions, S-ZrO_2 possesses distinct advantages over many solid acids. It is reusable and can be used in powder form and pelletised form.

The alkylation of diphenyl oxide (DPO) with a number of olefins, alcohols, and benzyl chloride leads to commercially important products, for instance, heat transfer fluids and perfumery compounds. Particularly the alkylation of diphenyl oxide with benzyl chloride has not been reported in the literature, and the alkylated product has potential uses as a heat-transfer fluid among others. Thus, it was thought worthwhile to study systematically the Friedel−Crafts alkylation of diphenyl oxide with benzene chloride (using sulphated zirconia as a catalyst) including kinetics and mechanism.

Experimental Section

Experimental Setup and Methodology. A 100-mL glass reactor (internal diameter 5 cm and height 10 cm) which was fully baffled was employed. It was provided with a six-bladed turbine impeller located at 0.5 cm from the bottom of the reactor and a reflux condenser. The desired speed of agitation of the reaction mixture was achieved by controlling the speed of stirrer motor with a regulator. An electrically heated oil bath was used to heat the reactor. The temperature of the bath was maintained by using a temperature controller. Standard experiments were carried out by using 0.07 mol of diphenyl oxide (11.9 g) and 0.01 mol of benzyl chloride (1.265 g). A catalyst loading of 50 kg/m^3 of total reactants (0.064 g) was used. The liquid-phase volume was 12.8 mL. The reactions were carried out at 90 °C for 1 h. A speed of agitation of 20 rps rpm was employed for the reaction. Samples were collected periodically.

Analytical Method. The samples were analysed by gas chromatography (Chemito 8510 model with a flame ionisation detector). A 2 m × 3.2 mm internal diameter stainless steel column packed with Chromosorb WHP impregnated with 10% SE-30 was used for analysis. Synthetic mixtures

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of the authentic components were used for calibration and quantification of the data.

Reagents. Diphenyl oxide was obtained from Hardillia Chemicals Ltd., Mumbai, India. Benzyl chloride was procured from M/s s.d.Fine Chemicals Pvt. Ltd., Mumbai, India. Zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$) of AR grade was obtained from M/s. Loba Chemie, Mumbai, India. Sulphuric acid of AR grade, used as sulphating agent, and ammonia solution, used for the preparation of zirconium hydroxide, were obtained from M/s s.d. Fine Chemicals Ltd., Mumbai, India.

Preparation of the Catalyst. Sulphated zirconia was prepared by a process developed in this laboratory.[4,6,7] A known amount of zirconium oxychloride was dissolved in deionised water and filtered. The filtrate and aqueous ammonia solution were placed into two different separating funnels and were simultaneously added to a beaker, at controlled flow rates under constant stirring, while maintaining the pH of the mixture solution at ~9−10. By this process, a white zirconium hydroxide [$Zr(OH)_4$] precipitate was obtained. After the precipitation was complete, it was kept for 1 h for digestion and filtered. The solids were washed with deionised water until no ammonia and chloride ions were detected in the washings, the absence of which was confirmed through the phenolphthalein and silver nitrate tests, respectively. The white precipitate of zirconium hydroxide was then dried in an oven at 393 K for 24 h. The dried cake was crushed to small particles. Sulphation of this hydrous zirconia was done by percolating 1 N H_2SO_4 solution through it, taken as 15 cm^3/g of solids. The sulphated zirconium hydroxide was then calcined in air at 923 K for 3 h to obtain the final catalyst. The Hammet acidity function H_0 of sulphated zirconia is −16.0, and it is a known solid superacid with both Brønsted and Lewis acidity.[7] The surface area[6] of the catalyst is 102 m^2/g.

Results and Discussion

Reaction Chemistry. The Friedel−Crafts alkylation of diphenyl oxide (B) with benzyl chloride (A) in the presence of sulphated zirconia catalyst leads to the formation of an isomeric mixture of benzyl-diphenyl oxide (MW 260) which was confirmed through GC−MS and FTIR. The reaction scheme is shown in Figure 1 In the presence of S-ZrO_2 catalyst, benzyl chloride is protonated, and the benzyl carbenium ion or carbocation so formed then combines with diphenyl oxide in the ortho or para position to give an isomeric mixture as the product **(**Figure 2).

Effect of HCl Acid Generated in Situ. The HCl generated in situ is desorbed from the reaction mixture at the reaction temperature, and any small quantity of dissolved HCl does not catalyse these types of reactions.[4,6] In the current study, nitrogen was purged continuously through the mixture with the result that there was no effect on the conversion of benzyl chloride at 90 °C. HCl has poor solubility in the reaction mixture at higher temperatures, and any trace amount left is not sufficient to produce any reaction.

A standard experiment was done wherein the reaction was started with only DPO and benzyl chloride under otherwise identical conditions at 90 °C. A sample after 2 h did not show any conversion of benzyl chloride. The catalyst was then added, the reaction was continued with the result that the reaction had proceed smoothly, and within 10 min there was a conversion of 29.5% of benzyl chloride. This was in conformity with the usual experiment. Then 2 mL of sample was pipetted out carefully without any catalyst particles in it, this solution was placed in a test tube to which a specially

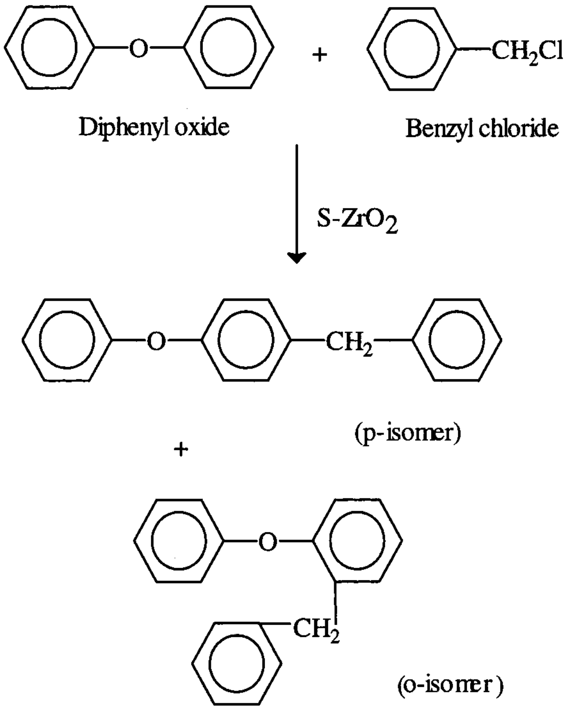
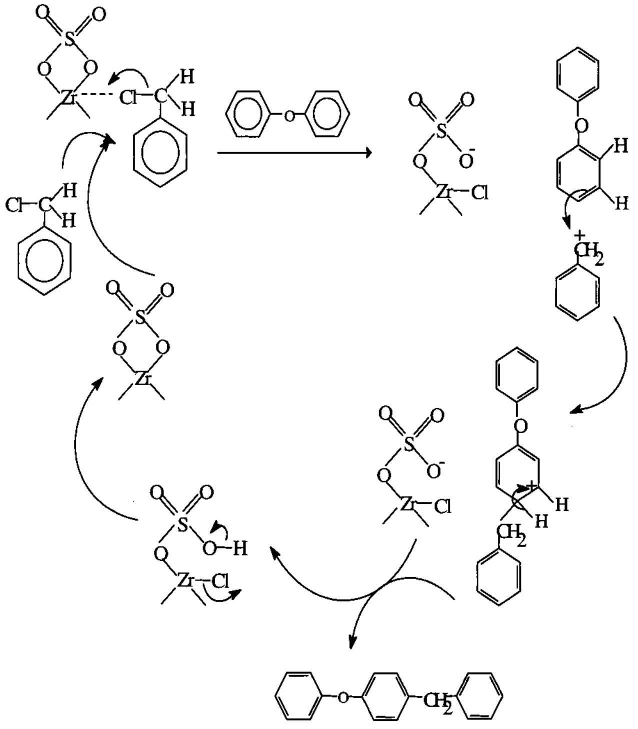


Figure 1. **Reaction scheme for the reaction between diphenyl oxide with benzyl chloride over sulphated zirconia catalyst.**



(same mechanism is applicable for o-isomer)

Figure 2. **Mechanism of the reaction between benzyl chloride with diphenyl oxide over sulphated zirconia.**

necked condenser was attached, and the assembly was placed in the oil bath at the same temperature. Simultaneously the reaction was continued in the reactor, and sampling was done after 10 min. The test tube liquid and the reaction mixture were analysed to find that the test tube sample had the same composition as in the beginning, whereas the sample from the reactor showed a conversion of 48.2%, which was little more than the standard experiment. This suggested that the reaction between DPO and benzyl chloride did not proceed without sulphated zirconia whose loading per unit volume of liquid phase had increased due to withdrawal of a large sample. Thus, it was concluded that this was a true heterogeneous reaction and also that HCl did not catalyse the reaction.

Effect of External Mass Transfer. This is a typical solid−liquid slurry reaction involving the transfer of benzyl chloride (A) and diphenyl oxide (B) to the catalyst wherein external mass transfer of reactants to the surface of the catalyst particle, followed by intraparticle diffusion, adsorption, surface reactions, and desorption, takes place. The influence of external solid−liquid mass-transfer resistance must be ascertained before a true kinetic model could be developed.[4] Thus, experimental and theoretical analyses were done.

The reaction studied in this case involves two reactants in organic phase, which react on the surface of the catalyst to form liquid-phase (organic) products at the reaction temperature chosen. The overall reaction can be presented as follows:

$$\mathrm{A} + z\mathrm{B} \rightarrow \mathrm{D} + \mathrm{E} \qquad (1)$$

where A and B are the reactants and D and E are the products. z is the stoichiometric coefficient of B.

At steady state, the rate of mass transfer per unit volume of the liquid phase (kmol·m^{-3}·s^{-1}) is given by:

$$R_A = k_{SL-A}a_p\{[A_0] - [A_s]\} \qquad (2)$$

(rate of transfer of A from bulk liquid to external surface of the catalyst particle)

$$= zk_{SL-B}a_p\{[B_0] - [B_s]\} \qquad (3)$$

(rate of transfer of B from the bulk liquid phase to the external surface of the catalyst particle)

$$= r_{obs} \qquad (4)$$

= rate of reaction within the catalyst particle.

Equation 4 could be represented by a Langmuir−Hinshelwood−Hougen−Watson-type or power law model with or without the effectiveness factor, η, to account for the intraparticle diffusion resistance.

Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms were put forward.[4] When the external mass-transfer resistance is small, then the following inequality holds,

$$\frac{1}{r_{obs}} >> \frac{1}{k_{SL-A}a_p[A_0]} \quad \text{and} \quad \frac{1}{k_{SL-B}a_p[B_0]} \qquad (5)$$

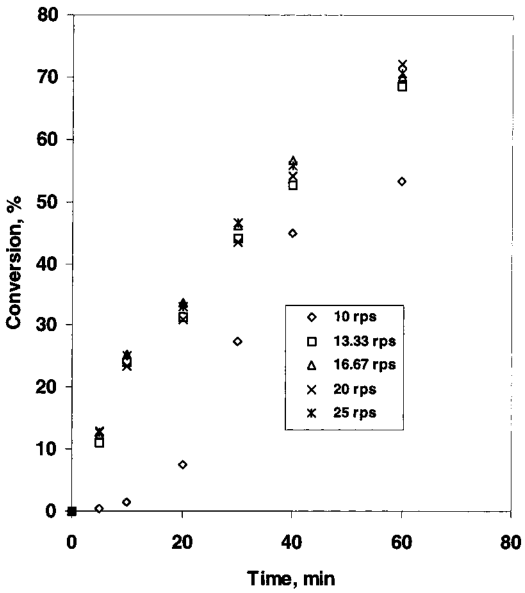


Figure 3. **Effect of speed of agitation on conversion of benzyl chloride.**

The observed rate r_{obs} could be given by three types of models wherein the contribution of intraparticle diffusion resistance could be accounted for by incorporating the effectiveness factor, η. These models are (a) the power-law model if there is very weak adsorption of reactant species, (b) the Langmuir−Hinshelwood−Hougen−Watson model, and (c) the Eley−Rideal model.

Since diphenyl oxide (B) was used in large excess over benzyl chloride (A), there was a chance of external resistance for the transfer of benzyl chloride from the bulk liquid phase to the external surface of the catalyst particle. Therefore, the speed of agitation was varied under otherwise identical condition for a particle size of $<90\ \mu$m. The effect of speed of agitation was studied at a catalyst loading of 50 kg/m^3 at 90 °C over the range of 10−25 rps. Figure 3 shows the conversion of benzyl chloride with time. It is seen that the conversion remains practically the same at and beyond a speed of 16.67 rps, which indicates the absence of external solid−liquid mass-transfer resistance. Theoretical analysis was also be done to ensure that the external mass-transfer resistance was indeed absent as delineated below.

The liquid-phase diffusivity values D_{AB} (benzyl chloride in diphenyl oxide) and D_{BA}(diphenyl oxide in benzyl chloride) were calculated by using the Wilke−Chang equation.[17] The values obtained at 90 °C are as follows:

$$D_{AB} = 2.388 \times 10^{-9}\ \mathrm{m^2/s}$$

$$D_{BA} = 2.7877 \times 10^{-9}\ \mathrm{m^2/s}.$$

The average particle size used in all experiments was 46.8 μm which was measured by an image analyser (Tracor Northern 8500, U.S.A.). Thus, the particle surface area per unit liquid volume could be calculated from $a_p = 6w/\rho_p d_p$ as 1203 m^{-1} [where $w = 50$ kg/m^3 of solid loading, $\rho_p = 5330$ kg/m^3, $d_p = 46.8\ \mu$m].

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(17) Reid, R. C.; Prausnitz, M. J.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

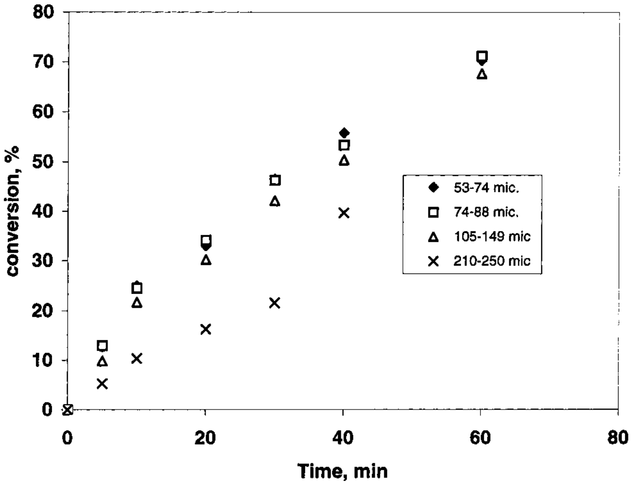

Figure 4. **Effect of particle size on conversion of benzyl chloride.**

Thus, the contribution of external mass-transfer coefficient could be calculated. The solid−liquid mass-transfer coefficients for A and B, given as k_{SL-A} and k_{SL-B}, respectively, were determined by the Sherwood number correlation. To be on the safe side, the limiting value of the Sherwood number was taken as 2. The actual value is far greater than 2 due to intense agitation.

Thus, from the Sherwood number, $Sh = k_{SL}d_p/D$ the solid−liquid mass-transfer coefficients for A and B are calculated as:

$$k_{SL-A} = 1.02 \times 10^{-4}\ \text{m/s} \quad \text{and} \quad k_{SL-B} = 1.19 \times 10^{-4}\ \text{m/s}$$

Substituting these values in eq 5,

$$\frac{1}{k_{SL-A}a_p[A_0]} = 10.4\ \text{m}^3\text{s/kmol}$$

and

$$\frac{1}{k_{SL-B}a_p[B_0]} = 1.27\ \text{m}^3\text{s/kmol}$$

$$\frac{1}{r_{obs}} = 3.71 \times 10^3\ \text{m}^3\text{s/kmol}$$

From these values it is clear that the conditions given by eq 5 are satisfied. That is, the rate of solid−liquid mass transfer is much higher than the observed rate of the reaction, and it can be said that the reaction is either surface-reaction controlled or intraparticle-diffusion controlled. Thus, the effects of particle size were studied to find out which of the two was controlling. Further experiments were conducted at 20 rps to avoid attrition of the catalyst at higher speeds.

Effect of Particle Size. The particles of the catalyst were crushed and sieved. The effect of particle size was studied in the ranges 53−74, 74−88, 105−149, and 210−250 μm under otherwise identical conditions, and conversion versus time plots were made (Figure 4**)**. It is seen that for the particle size below 88 μm, the reaction rates were independent of the size, which in turn offers support that the intraparticle-diffusion resistance was absent and that the reaction is intrinsically kinetically controlled. This was further confirmed by invoking the Wiesz−Prater criterion.[18]

According to the Wiesz−Prater criterion if

$$\text{(i) } C_{wp} = -r_{obs}\rho_p R^2/D_e C_{AS} \gg 1$$

then the reaction is limited by severe internal diffusion resistance,

$$\text{(ii) } C_{wp} \ll 1$$

then the reaction is surface-reaction controlled.

In the present case, the observed value of $C_{wp} = 0.072$, and the reaction is surface-reaction controlled.

A further proof of the absence of the intraparticle-diffusion resistance was obtained through the study of the effect of temperature, and it will be discussed later.

Since both internal and external mass-transfer resistances were absent, further development was done by considering the adsorption, surface reaction, and desorption steps.

Development of Mechanistic Model and Kinetics of the Reaction. In the case of present studies, it is essential to understand the reaction mechanism to develop a suitable model. The initial rate data could be analysed on the basis of Langmuir−Hinshelwood−Hougen−Watson (LHHW) or Eley−Rideal mechanisms. For initial rate data, the following analysis is most appropriate.[9] The mechanism as shown in Figure 2 can be used to arrive at the LHHW type of mechanism.

1. Adsorption of benzyl chloride (A) on a vacant site S is given by:

$$\text{A} + \text{S} \overset{K_A}{\rightleftharpoons} \text{AS} \qquad \text{(a)}$$

Similarly adsorption of diphenyl oxide (B) on a vacant site S is represented by:

$$\text{B} + \text{S} \overset{K_B}{\rightleftharpoons} \text{BS} \qquad \text{(b)}$$

2. Surface reaction of AS with BS, in the vicinity of the site, leading to formation of benzyl diphenyl oxide (ES) on the site.

$$\text{AS} + \text{BS} \overset{K_2}{\rightleftharpoons} \text{ES} + \text{WS} \qquad \text{(c)}$$

Desorption of benzyl diphenyl oxide (ES), and HCl (WS)

$$\text{ES} \overset{1/K_E}{\rightleftharpoons} \text{E} + \text{S} \qquad \text{(d)}$$

$$\text{WS} \overset{1/K_W}{\rightleftharpoons} \text{W} + \text{S} \qquad \text{(e)}$$

The total concentration of the sites, C_t expressed as

$$C_t = C_S + C_{AS} + C_{BS} + C_{ES} + C_{WS}$$

or

$$C_t = C_S + K_A C_A C_S + K_B C_B C_S + K_E C_E C_S + K_W C_W C_S \qquad (9)$$

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(18) Fogler, H. S. *Elements of Chemical Reaction Engineering*; Prentice-Hall: Englewood Cliffs, 1986.

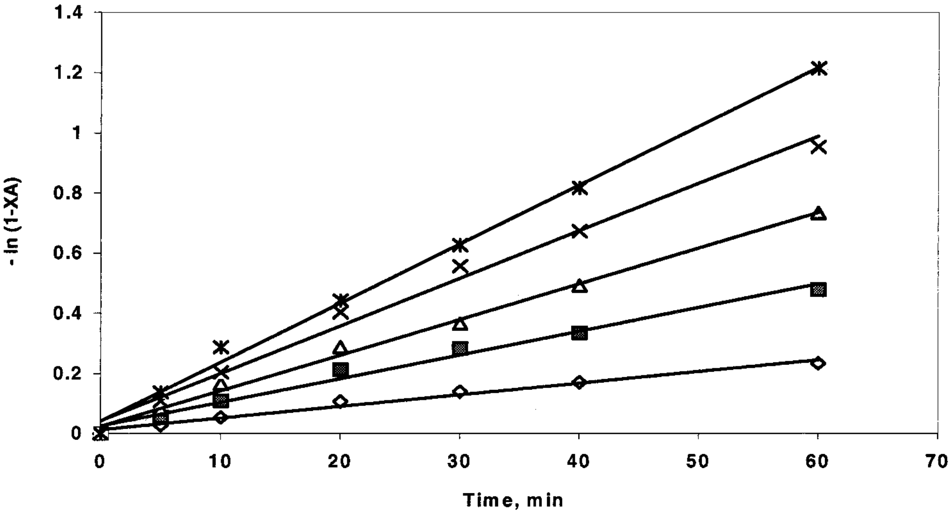

Figure 5. **Typical first-order reaction plot lines: effect of catalyst loading (∗, 50 kg/m³; ×, 40 kg/m³; △, 30 kg/m³; ■, 20 kg/m³; ◇, 10 kg/m³).**

or, the concentration of vacant sites,

$$C_S = \frac{C_t}{(1 + K_A C_A + K_B C_B + K_E C_E + K_w C_w)} \qquad (10)$$

If surface reaction (c) controls the rate of reaction, then the rate of reaction of A is given by

$$-r_A = -\frac{dC_A}{dt} = k_2 C_{AS} C_{BS} - k_2' C_{ES} C_{WS} \qquad (11)$$

$$-\frac{dC_A}{dt} = \frac{k_2\left\{K_A K_B C_A C_B - \dfrac{K_E K_W C_E C_W}{K_2}\right\} C_t^2}{(1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \qquad (12)$$

when the reaction is far away from equilibrium

$$-\frac{dC_A}{dt} = \frac{k_2 C_t^2 K_A K_B C_A C_B}{(1 + \sum K_i C_i)^2} \qquad (13)$$

$$= \frac{k_{R2} w C_A C_B}{(1 + \sum k_i C_i)^2} \qquad (14)$$

where $k_{R2}w = k_2 C_t^2 K_A K_B$; w is catalyst loading. If the adsorption constants are very small, then the above equation reduces to

$$-\frac{dC_A}{dt} = k_{R2} C_A C_B w \qquad (15)$$

Let $C_{B0}/C_{A0} = M$, the molar ratio of diphenyl oxide to benzyl chloride at time $t = 0$. Then eq 10 can be written in terms of fractional conversion as

$$\frac{dX_A}{dt} = k_{R2} w C_{Ao}(1 - X_A)(M - X_A) = k_1 C_{Ao}(1 - X_A)(M - X_A) \qquad (16)$$

which upon integration leads to:

$$\ln\{(M - X_A)/M(1 - X_A)\} = k_1 C_{Ao}(M - 1)t \qquad (17)$$

when M is other than unity.

For equimolar quantities of A and B, the integration of eq 10 yields the following

$$\frac{X_A}{1 - X_A} = C_{Ao} k_{R2} w t = k_1 t \qquad (18)$$

When $M \gg 1$, eq 12 leads to a pseudo-first-order kinetics; hence, upon integration it becomes,

$$-\ln(1 - X_A) = k_{R2} C_{Bo} w t = k_1 t \qquad (19)$$

where, $k_1 = k_{R2} C_{Bo} w$.

Thus, further experiments were done to study the effects of catalyst loading, concentration of reactants, and temperature to validate the theory.

Effect of Catalyst Loading. The catalyst loading based on the total volume of reaction mixture was varied at five different values from 10 to 50 kg/m³ at a mole ratio of DPO to benzyl chloride of 7:1. It was observed that both the rate of reaction and rate of conversion had increased with catalyst loading due to the increase in available sites. The concentration profile indicated a first-order profile, and hence typical plots of $-\ln(1 - X_A)$ versus time were made (Figure 5) for each catalyst loading to get the slopes k_1, the pseudo-first-order constant, which were in turn plotted against solid loading w (Figure 6) to get a linear relationship. This is due to the proportional increase in the number of active sites. The value of k_{R2} thus obtained from k_1 at 90 °C is 1.21×10^{-6} $\mathrm{m}\cdot^{6}\mathrm{kmol}^{-1}\cdot\mathrm{kg}^{-1}\cdot\mathrm{s}^{-1}$.

Effect of Mole Ratio. The effect of the mole ratio of the reactants was studied for different mole ratios of diphenyl oxide and benzyl chloride (7:1, 8:1, 10:1, and 12:1) under otherwise identical conditions (Figure 7). It was found that as the mole ratio of diphenyl oxide to benzyl chloride was changed, the conversion of diphenyl oxide remained practically the same, which shows zero-order dependence on diphenyl oxide concentration and a typical first-order dependence on benzyl chloride concentration.

Effect of Temperature. The effect of temperature was studied at five different temperatures under otherwise similar conditions (Figure 8). The conversion of benzyl chloride

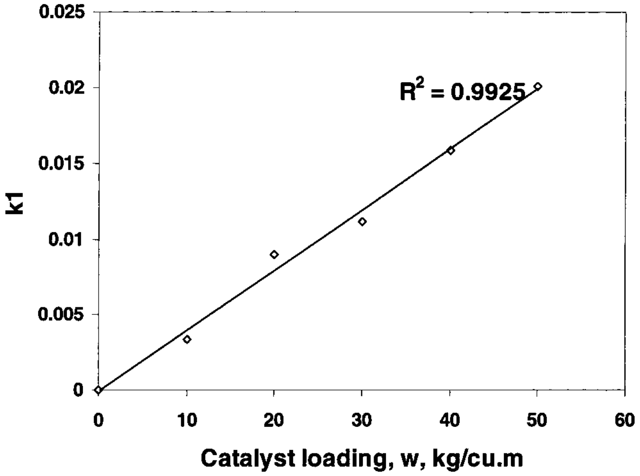

Figure 6. **Relationship berween k_1 (pseudo-first-order rate constant) and catalyst loading, w.**

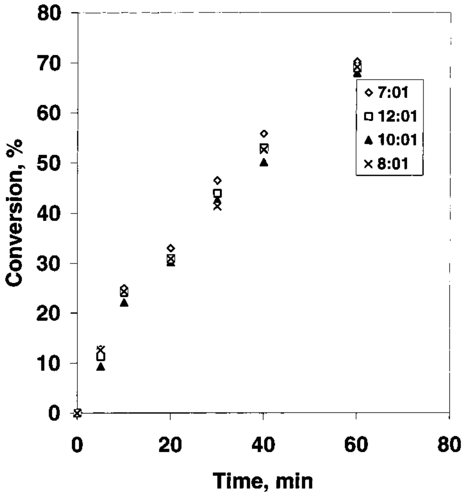

Figure 7. **Effect of mole ratio of DPO to benzyl chloride.**

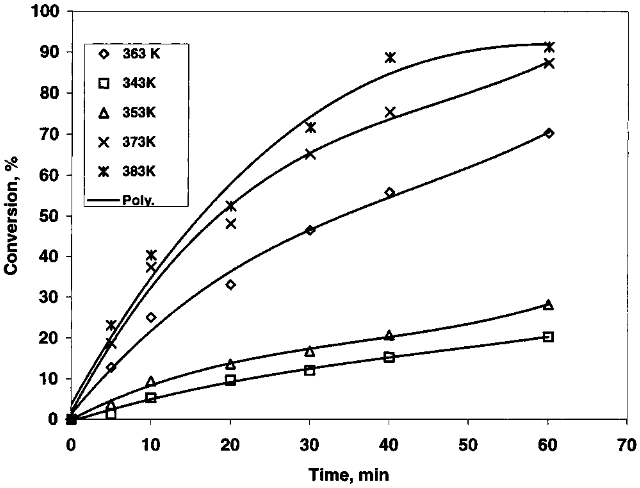

Figure 8. **Effect of temperature on conversion of benzyl chloride.**

increased with increase in temperature of the reaction. Correspondingly $-\ln(1 - X_A)$ versus time were plotted at each temperatures (Figure 9), and these slopes (k_1) were used to make the Arrhenius plot (Figure 10). From the slope of the curve the apparent activation energy was calculated. The

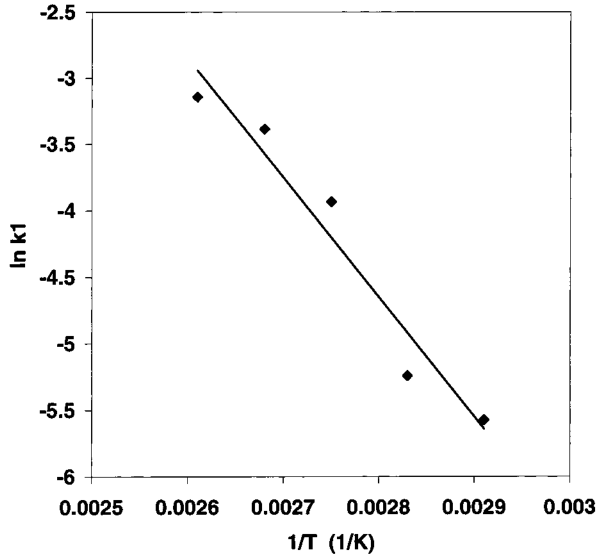

Figure 9. **Arrhenius plot.**

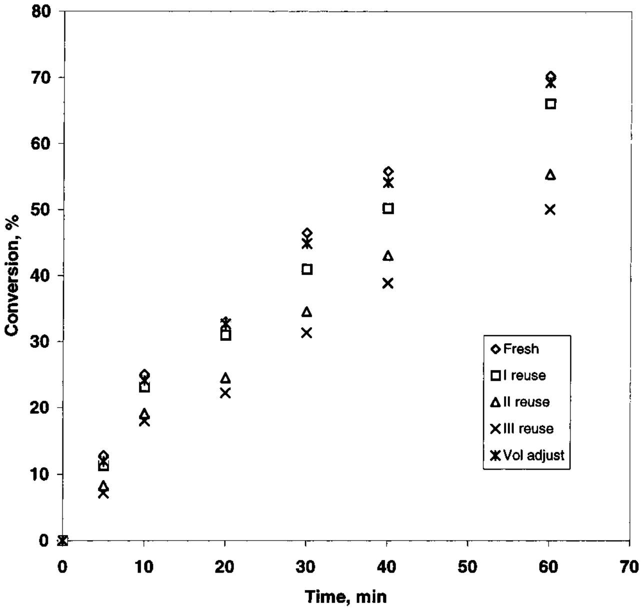

Figure 10. **Catalyst reuse and activity.**

activation energy was found to be 74.82 kJ/mol. The high value of activation energy again shows that the reaction was kinetically controlled and occurred at the surface of the reaction.

Thus, the kinetics of the reaction was established through the LHHW surface-reaction controlled mechanism in the absence of both internal and external mass-transfer resistances.

Effect of Catalyst Reuse. The reusability of the catalyst was studied by recycling the filtered and acetone-washed catalyst under otherwise identical conditions. Figure 10 shows the conversion of benzyl chloride against time, and that the conversion has been decreased from 66 to 50% from the fresh to the third reuse of the catalyst. There was attrition of the catalyst; hence; some catalyst was lost during filtration. Attrition has no effect on the acidity of the catalyst since it is on the pore surface and no acid sites are lost even though particle size is reduced. The batch size was doubled, and after the reaction the catalyst was filtered. There was a loss of 4.5% catalyst during filtration. Thus, in the next experiment, the volume of the reaction mixture was adjusted to make the catalyst loading, 50 kg/m^3, the standard value. It was found that the conversions were practically the same as in the previous run, thereby suggesting that there was no loss in activity.

Thus, it can be concluded that there was little decrease in the catalyst activity with reuse.

Conclusions

The Friedel−Craft alkylation of diphenyl oxide with benzyl chloride was studied by using sulphated zirconia as the catalyst. This catalyst is reusable. The effects of various parameters were studied on the rate of the reaction under otherwise similar conditions. It was seen that external mass-transfer resistance can be eliminated by providing adequate stirring and internal mass-transfer resistance was also absent. A LHHW model was tested which shows that the reaction is intrinsically kinetically controlled.

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NOMENCLATURE

A reactant species, benzyl chloride
a_p solid−liquid interfacial area, m^2/m^3 of liquid phase
$[A_0]$ concentration of A in bulk liquid phase, kmol/m^3
B reactant species, diphenyl oxide
$[B_0]$ concentration of B in bulk liquid phase, kmol/m^3
C_A concentration of A, mol/m^3
C_{A0} initial concentration of A in Bulk liquid phase, kmol/m^3
C_{AS} concentration of A at the catalyst surface, kmol/m^3
C_B concentration of B, kmol/m^3
C_{BS} concentration of B at the catalyst surface, kmol/m^3
C_{B0} initial concentration of B in bulk liquid phase, kmol/m^3
C_{wp} Wietz−Prater parameter, dimensionless
D reaction product
D_{AB} diffusion coefficient of A in B, m^2/s
D_{BA} diffusion coefficient of B in A, m^2/s
d_p diameter of the catalyst particle, m
D_e effective diffusivity, m^2/s
E reaction product
K_i equilibrium constants of various species i
k_1 pseudo-first-order rate constant, s^{-1}·m^3·kg-cat^{-1}
k_{R2} second-order surface reaction rate constant, m^3·kg-cat^{-1}·s^{-1}
k_{SL-A},k_{SL-B} solid−liquid mass-transfer coefficient for A and B, respectively
R radius of the catalyst particle, m
r_A rate of the reaction of A, kmol·m^{-3}·s^{-1}
r_{obs} observed rate of the reaction, kmol·kg-cat^{-1}·s^{-1}
w catalyst loading, kg/m^3 of liquid phase
X_A fractional conversion of A
η effectiveness factor
ρ_p density of the catalyst particle, kg/m^3

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