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Role of Benzyl Ether in the Inversion of Reactivities in Friedel-Crafts Benzylation of Toluene by Benzyl Chloride and Benzyl Alcohol

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Abstract : In the inversion in the reactivities and selectivities of benzyl chloride (BnCl) and benzyl alcohol (BnOH) in a single pot Friedel-Crafts benzylation with toluene, there is not only a preferential adsorption of benzyl alcohol on the solid acid catalyst but also a second preference to the adsorption of benzyl ether (BE) formed in-situ. The order of prefential adsorption is BnOH > BE > BnCl. Copyright © 1996 Elsevier Science Ltd

We reported[1] in this Journal that the intriguing phenomenon of inversion in the relative reactivities and selectivities of benzyl chloride (BnCl) and benzyl alcohol (BnOH) in the Friedel-Crafts benzylation of toluene in presence of solid acid catalysts is due to the preferential adsorption of benzyl alcohol over benzyl chloride in a single pot experiment. Further, this inversion phenomenon was not restricted to the "Clayzic" catalyst as earlier reported by Laszlo and co-workers[2-5] and that other non-sieving catalysts such as Filtrol-24 and sulfated zirconia (S-ZrO_2) were very effective. Interestingly, Laszlo and Davister[6] also reported subsequently that indeed preferential adsorption was responsible for the inversion. However, we have found that for the single pot benzylation of toluene with benzyl chloride and benzyl alcohol, the sequence in preferential adsorption is further altered due to the presence of benzyl ether (BE) generated in-situ or added externally.

During the process of studying the kinetics of the independent and single pot parallel reactions at different temperatures, a peculiar behaviour in the product distribution, particularly at 100^0C and above, was noticed and therefore the current investigation was undertaken.

In a typical experiment, for independent reactions the desired quantity of BnCl (0.05 gmol) or benzyl alcohol (0.05 gmol) was taken separately in a measured quantity of toluene (0.5 gmol) in a mechanically agitated contactor equipped with reflux condenser and pitched-bladed turbine impeller. For the single pot reactions, both BnCl (0.025 gmol) and BnOH (0.025 gmol) or BE (0.025 gmol) were taken together with toluene (0.5 gmol). Then the mixture was brought to the desired reaction temperature under agitation and the required amount of pre-dried catalyst (20% w/w) was added. The reaction was carried out for 4 hrs. Analysis of the reaction mixture was done by GC with 2m x 1/8" S.S. column packed with OV-17(10%) on Chromosorb WHP by using FID.

In a single pot reaction of BnCl and BnOH with toluene at 100 ^{0}C, it was observed after 1 hr that no BnOH was present in the reaction mixture (Fig. 1) and BE was generarted by the dehydration of benzyl alcohol. At the same time no BnCl had reacted during this period. The preferential adsorption of BnOH over BnCl was quite evident. However, thereafter, both BnCl and benzyl ether (BE) were found to react simultaneously with toluene and after 1.5 hrs, no BE was left in the reaction mixture and only 28.5% of BnCl had reacted. The reaction of BnCl with toluene was continued upto 4 hrs as shown in Fig. 1.

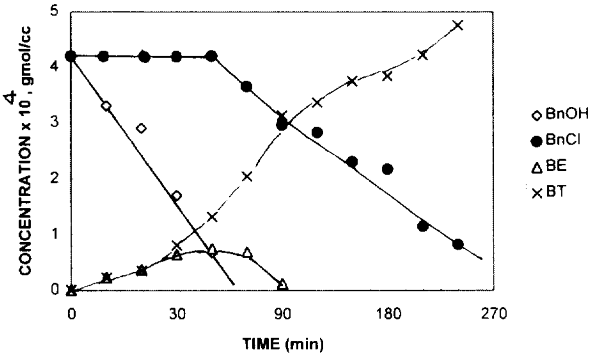

FIG. 1 : Mixture (BnCl & BnOH), Catalyst; S-ZrO$_2$, Loading; 20% w/w, Temperature; 100^{0}C, Stirrer Speed; 1000 rpm, BT; Benzyl toluene or alkylated product (*o, m,* or *p*).

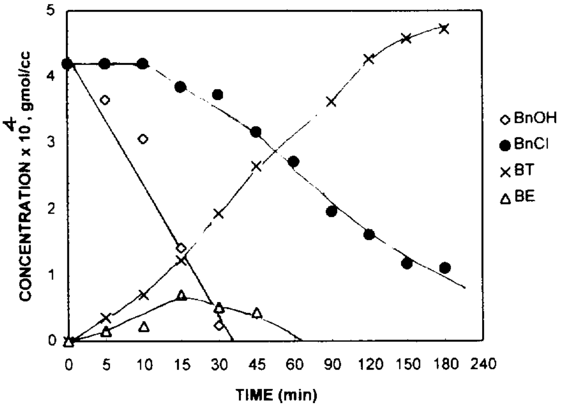

FIG. 2 : Mixture (BnCl & BnOH), Catalyst; S-ZrO$_2$, Loading; 20% w/w, Temperature; 110^{0}C, Stirrer Speed; 1000 rpm, BT; Benzyl toluene or alkylated product (*o,m,* or *p*).

The above experiment was repeated at a higher temperature of 110^0 C as shown in Fig. 2 and the same behaviour as before is observed as regards the preferential adsorption and reaction.

In the mixture, BE reacts preferentially and is strongly adsorbed onto the catalytic sites and prevents any adsorption of BnCl thus depriving the latter from reacting with toluene. Only when some sites are vacant due to almost total depletion of BE by reaction, for the given small quantity of catalyst, the BnCl molecules get a chance to adsorb and react. However, for small concentrations of BE in comparison with BnCl, this fact was not noticed in the experimental results (Fig. 1 and 2).

The above hypotheses had to be verified in order to define the precise role of BE as a co-reactant in the preferential adsorption phenomenon. It was necessary to monitor the concentration profile of BE which is produced in-situ. A new set of experiments was done with the two different alkylating agents involving BE and BnCl (Fig. 3).

However, a different strategy was followed in that BnCl (0.05 gmol) was initially taken alongwith toluene and the experiment was started at 90°C with 20% w/w catalyst loading (Fig. 3). The reaction was monitored as a function of time. A first order kinetic type of disappearance of BnCl was noticed. After 1 hr, BE (0.025 gmol) was added. Further monitoring of the reaction showed that only BE was consumed to a large extent and the rate of consumption of the ether was linear with reference to time thereby indicating a zero order dependence. This illustrates that the ether prohibited the reaction of BnCl and there is preferential adsorption of the ether in comparison with BnCl.

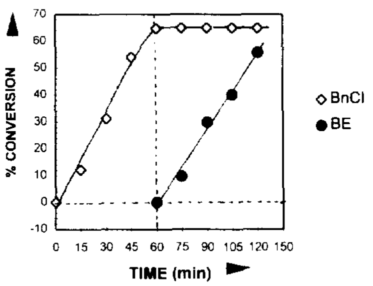

FIG. 3 : BnCl taken initially and addition of BE after 1 hr.

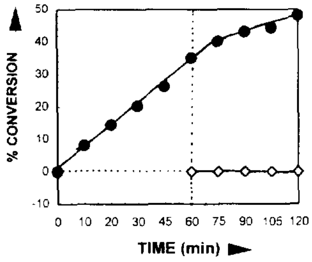

FIG. 4 : BE taken initially and addition of BnCl after 1hr.

To bolster the above arguments the order of adding the benzylating agents in the above experiment was then reversed and BE (0.05 gmol) was initially taken in the reactor (Fig. 4). The rate of reaction of BE was slower (Fig. 4) than that of BnCl taken alone (Fig. 3). After 1 hr, the percent conversion to benzyltoluene was only 30%. Then 0.025 gmol of BnCl was added to the reaction mixture to find that the reaction of BE continued further but no BnCl had reacted. The rate of reaction of BE was apparently zero order. It thus appears that the concentration of BE was sufficient to occupy all the sites leaving no vacant sites for BnCl adsorption. The kinetics of the reaction followed the Langmuir Hinshelwood model modified by the Eley-Rideal mechanism wherein the adsorbed benzylating species reacts with toluene from the liquid phase in the pore space. In the single pot situation, the equation is

$$r_i = \frac{k_i w C_i}{1 + \Sigma K_{ai} C_i} \qquad (i = 1,2,3) \qquad (1)$$

where r_i, k_i, C_i and K_{ai} are the rate of reaction, rate constant (incorporating concentration of toluene), concentration and adsorption equilibrium constant for species I, respectively. w is the catalyst loading per unit volume of liquid phase. Due to the strong adsorption of BnOH (1) over BE (2) and BnCl (3) the adsorption term in the denominator of eq. (1) becomes equal to $K_{a1}C_1$ and hence a zero order dependence on concentration of BnOH results. When BE and BnCl are in the single pot such that $C_2 >> C_3$, the rate is once again zero order in the concentration of BE because of the preferential strong adsorption of BE. In the case of BnCl, whether alone or in a single pot with BnOH/BE, the kinetics is represented by a first order equation due to the weak adsorption of BnCl and complete consumption of BnOH/BE, thereby making the denominator in eq. (1) as unity.

When the single pot experiment as depicted in Fig. 1 was repeated and after 15 minutes, the same amount of BE as generated in-situ was added., the concentration of BE increased correspondingly without any reaction of BE or BnCl. When equimolar quantities of BnOH, BE and BnCl were taken together with toluene, once again it was observed that BnOH reacts first and the concentration of BE increases beyond that added initially. After BnOH had reacted leaving some sites vacant, BE starts reacting.

Thus, the preferential adsorption order for the benzylation of toluene with benzyl chloride, benzyl alcohol and benzyl ether either generated in-situ or added externally in a single pot situation is,

$$\text{BnOH} > \text{BE} > \text{BnCl}. \qquad (2)$$

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