Tetrahedron Letters, Vol. 34, No. 3, pp. 529-532, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

Inversion of the Relative Reactivities and Selectivities of Benzyl Chloride and Benzyl Alcohol in Friedel-Crafts Alkylation with Toluene Using Different Solid Acid Catalysts : An Adsorption Related Phenomenon

Ganapati D. Yadav*, Tushar S. Thorat and Pramod S. Kumbhar

Department of Chemical Technology, University of Bombay, Matunga,
BOMBAY — 400019, INDIA
Fax : 91-022-414 5614

Key Words : selectivity; co-reactant; Friedel-Crafts; acid catalyst; adsorption.

Abstract : The Friedel-Crafts alkylation of benzyl chloride and benzyl alcohol, separately as well as in a single pot, with toluene as an alkylating agent in presence of different solid acid catalysts has been investigated to find that the inversion of relative reactivities is due to a preferential adsorption phenomenon.

Laszlo and co-workers[1-4] have demonstrated through a series of publications in this Journal how the rates of two parallel reactions can be dramatically altered, in comparison with the case when these reactions are run separately, by using "clayzic" catalyst. Of particular interest to us is the Friedel-Crafts alkylation of benzyl chloride and benzyl alcohol with toluene, which we have investigated with a variety of solid acidic catalysts. And we would like to report here that the phenomenon observed here is not restricted to the "clayzic" type of catalyst alone and further that this attribute of the "clayzic" catalyst that appeared to act as a microreactor capable of dynamic sieving, can be well explained in terms of preferential adsorption.

In our experiments we have used a number of solid acidic catalysts, namely, superacidic sulfated zirconia (S-ZrO_2), Filtrol-24, a clay catalyst and Amberlyst-15, an ion-exchange resin, which all have very good activity for the alkylation reaction[5].

Benzyl chloride (BnCl) and benzyl alcohol (BnOH) were reacted separately by taking 0.05 gmol of each. Whereas a mixture of benzyl chloride and benzyl alcohol in an equimolar quantity of 0.025 gmol each, were reacted with toluene (0.5 gmol) at appropriate temperatures with a catalyst loading of 20 W/W%. Analysis of the reaction mixture was done by GC with 2m x 1/8'' S.S. column of OV-17(10%) on Chromosorb WHP by using FID.

Table 1 summarises the experimental results. With sulfated zirconia and Filtrol-24, when reacted separately, benzyl chloride is more reactive than benzyl alcohol. Benzyl alcohol in addition to alkylation gives benzyl ether (BE) as a major side product which again gets converted to the alkylated product (o,m, or p). On the contrary, in the mixture benzyl alcohol reacts first and after it is completely consumed benzyl chloride starts reacting with toluene, which is similar to the behaviour reported by Laszlo et al. However, the sulfated zirconia and Amberlyst-15 catalysts are not clay-type catalysts and have totally different pore size distributions and surface areas. Thus, the inversion of reactivities may not be related to pore structural effects which are likely to be present in sieving-type catalyst. In the absence of any intraparticle diffusional limitations, the parallel reactions of benzyl chloride and benzyl alcohol with excess toluene in a single pot encounter three steps in series for each, namely, adsorption of the reactive species on the catalytic site, surface reaction of the adsorbed species with toluene, followed by desorption of the products. Since the same type of active sites are responsible for the two parallel reactions, the total number of sites available for adsorption will be distributed between BnCl and BnOH according to the relative magnitudes of the adsorption equilibrium constants for each. The individual rates of reactions will be governed by the slowest of the three steps in each case and the selectivities will depend on the relative concentrations of the adsorbed species on the catalyst surface. Analysis of data in Table 1 showed that the kinetics of individual reactions could be expressed by a single site Langmuir-Hinshelwood model and should also be applicable to the parallel reactions in the same pot.

$$r_i = \frac{wk_iC_i}{1 + K_{ai}C_i} \qquad i = 1,\ 2 \text{ (Separate)} \qquad (1)$$

$$r_i = \frac{wk_iC_i}{1 + \Sigma K_{ai}C_i} \qquad \text{(Parallel)} \qquad (2)$$

where r_i, k_i, C_i and K_{ai} are the rate of reaction, rate constant, concentration and adsorption equilibrium constant for species i (benzyl chloride - 1, benzyl alcohol - 2), respectively and w is the catalyst loading per unit volume of liquid phase.

In the case of reaction of BnCl alone, it was found that since BnCl is weakly adsorbed, the terms in the denominator approach unity, and the rate is governed by the first order kinetics. However, in the case of BnOH alone, the $K_{a2}C_2$ is very large in comparison with one, in the denominator, and hence the rate of reaction of BnOH becomes independent of concentration of BnOH and is equal to (wk_2/K_{a2}).

For the case of parallel reactions of BnCl and BnOH with toluene, in the same reactor, it is observed that only BnOH reacts with toluene and the rate of reaction is independent of concentration of BnOH. In the mixture, BnOH is preferentially and 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 BnOH by reaction, for the given small quantity of catalyst, the BnCl molecules get a chance to adsorb and react. This preferential adsorption phenomenon was found to be repeated at a higher temperature. For instance, with sulfated zirconia as catalyst, in the mixture of BnCl and BnOH, at 80°C, there was no conversion of BnCl after 30 minutes while 40.92% BnOH had reacted. Similar experiment at 100°C showed during the same time, 8.96% BnCl and 82.56% BnOH had reacted. Thus, temperature had a pronounced effect on the reaction of BnOH because both rate constant and adsorption equilibrium constants being higher led to much higher rates, whereas whaterver little BnCl was adsorbed got a chance to react. Again the entry in Table 1 for the same system at 100°C, reveals that much before 90 minutes all BnOH had reacted thereby allowing BnCl to get adsorbed and react on the surface.

The evidence for preferential adsorption of BnOH in comparison with BnCl was further provided by carrying out adsorption experiments as shown in Table 2. In this typical experiment, the catalyst, Filtrol-24 (1.26g) was taken in a reaction mixture of BnCl (0.05 gmol) and toluene (0.5 gmol) at 80°C and the reaction progress was monitored. At the end of 1.5 hrs, when 27.90% BnCl had reacted, BnOH (0.025 gmol) was added and within a minute a sample was withdrawn to find that 8.30% BnOH had reacted. It was observed that within next 1 hr, practically no BnCl had reacted while 100% BnOH was converted. Further progress of the reaction was monitored to find that the reaction of BnCl with toluene had once again commenced because there was no BnOH present on the sites. After 50.24% conversion of BnCl which was at 3.5 hr from the beginning, further quantity of BnOH (0.025 gmol) was added to see whether the same behaviour would be repeated. Once again it was found that no reaction of BnCl had occurred during the next one hour while almost all BnOH had reacted. This again demonstrates that only when the BnOH had been consumed from the adsorbed sites, BnCl gets a chance to adsorb and react.

We introduced another interesting variation of the above said experiment wherein purposely intraparticle diffusional resistance was superimposed. In a quiscent pool of BnCl (0.025 gmol) containing Filtrol (1.176g)

Table 1. Results of the Reaction between Toluene and Benzyl Chloride/Benzyl Alcohol and their Mixture over Various Solid Acid Catalysts

Catalysts	**Temp °C**	**Time min**	**% Conversion**		**Product Distri.**	
			BnCl	**BnOH**	**Alkylated**	**BE**
S-ZrO$_2$	80	90	49.92	—	100.00	—
	80	90	—	16.68	31.07	68.93
	80	30	0.0	40.92	47.37	52.62
	80	90	12.12	80.72	55.37	44.63
S-ZrO$_2$	100	30	100.00	—	100.00	—
	100	30	8.96	82.56	64.42	35.57
	100	90	69.47	100.00	100.00	0.0
Filtrol-24	80	90	52.00	—	100.00	—
	80	90	—	19.26	51.56	48.44
	80	90	0.0	100.00	84.78	15.22
Amberlyst-15	80	90	1.36	—	1.36	—
	80	90	—	39.60	44.05	55.95
	80	90	0.00	87.51	78.91	21.09

Table 2. Results of the Adsorption Experiments between Benzyl Chloride and Benzyl Alcohol for Alkylation by Toluene over Filtrol-24 at 80°C.

Time (hrs)	**% Conversion**	
	BnCl	**BnOH**
0	0	—
0.5	7.42	—
1.0	20.80	—
1.5[a]	27.90[a]	8.30[a]
1.75	27.52	56.80
2.0	28.30	74.52
2.5	32.14	100
3.0	50.28	—
3.5[b]	50.24[b]	14.48[b]
3.75	50.40	37.60
4.25	50.32	60.0
4.5	50.52	96.80
5.0	65.54	100

[a] : At the end of 1.5 hrs, 0.025 gmol of benzyl alcohol was added to the reaction mixture, at which benzyl chloride concentration was 0.036 gmol and within a minute the sample was withdrawn for analysis.

[b] : At the end of 3.5 hrs, again 0.025 gmol of benzyl alcohol was added at which benzyl chloride concentration on the catalyst surface had declined to 0.0248 gmol, and after 2 minutes a sample was withdrawn.

at 80°C, a preheated mixture of BnOH (0.025 gmol) and toluene (0.5 gmol) at 80°C was added and samples were periodically withdrawn from this unagitated reaction mixture. The analysis showed that even after 3 hr only BnOH (72.4%) had reacted without any reaction of BnCl. This further demonstrates that the preferential adsorption of BnOH in comparison with BnCl is responsible for this behaviour.

To bolster the above arguments, we conducted an experiment in which BnCl and BnOH (0.1 gmol each) with 1.176 g Filtrol-24 were agitated at 80°C and a stoichiometrically deficient quantity of toluene (0.1 gmol) was added to find that only BnOH had reacted because the catalyst surface was fully adsorbed with BnOH, leaving no vacant sites for BnCl.

For the sake of comparison, Table 1 also includes our results with Amberlyst-15 catalyst with which BnOH is already more reactive than BnCl, when both are reacted separately. The single pot parallel reactions showed a total selectivity to BnOH with no reaction of BnCl. These results have no bearing on the issue discussed before on the preferential adsorption.

In summary, the inversion of relative reactivities in the Friedel-Crafts alkylation of BnCl and BnOH with toluene is related to preferential strong adsorption of BnOH on the solid acid catalysts.

Acknowledgement:

Financial support for this work was provided by CSIR, New Delhi (Grant No. 2(346)/91-EMR-II) to GDY).

References :

1. Laszlo, P.; Cornelis, A.; Dony, C.; Nsunda, K.M., *Tetrahedron Lett.*, **1991**, *532*, 2903-2904.
2. Laszlo, P.; Montaufier, M.T., *Tetrahedron Lett.*, **1991**, *32*, 1561-1564.
3. Cornelis, A.; Dony, C.; Laszlo, P.; Nsunda, K.M., *Tetrahedron Lett.*, **1991**, *32*, 2901-2902.
4. Cornelis, A.; Dony, C.; Laszlo, P.; Nsunda, K.M., *Tetrahedron Lett.*, **1991**, *32*, 1423-24.
5. Rajadhyaksha, R. A.; Chaudhari, D. D., *Ind. Eng. Chem. Res.*, **1987**, *26*, 1743-1746.

(Received in UK 2 September 1992)