Reactions of Benzyl Alcohol over Oxide Catalysts: A Novel Condensation to Form Anthracene

K. GANESAN AND C. N. PILLAI[1]

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

A novel heterogeneously catalyzed condensation of benzyl alcohol to form anthracene is reported. The reaction involves an orthoalkylation of a surface benzyl oxide species by the benzyl cation from a neighboring benzyl oxide to form o-hydroxymethyldiphenylmethane which undergoes cyclodehydration followed by aromatization to yield anthracene. Reactions have been carried out with alumina and modified alumina catalysts (fluorided and sodium ion-impregnated), HY-zeolite, phosphotungstic acid, and silicotungstic acid. Mechanistic features of the reaction are discussed. A simple and efficient synthesis of anthracene from benzyl alcohol over HY-zeolite is also described. © 1989 Academic Press, Inc.

INTRODUCTION

Benzyl alcohol undergoes dehydration to dibenzyl ether and water and disproportionation to benzaldehyde, toluene, and water, over alumina, at around 300°C (*1–3*).

$$2\ PhCH_2OH \xrightarrow[-H_2O]{Al_2O_3} PhCH_2OCH_2Ph$$

$$\Big\downarrow Al_2O_3$$

$$2\ PhCH_2OH \xrightarrow[-H_2O]{Al_2O_3} PhCHO + PhCH_3$$

In the course of a study of these reactions, it was observed that at high temperatures anthracene was formed in substantial quantities. While there are reports on the formation of anthracene from benzyl alcohol and related molecules in the presence of aluminium chloride (*4, 5*), this reaction under heterogeneous catalysis in the vapor phase does not seem to have been reported. Simple alkylation of aromatics by alcohols in the presence of alumina, zeolites, etc., is also known (*6–9*). The present paper describes the details of a study of the formation of anthracene from benzyl alcohol over oxide catalysts.

EXPERIMENTAL

Preparation and Characterization of Catalysts

The alumina catalyst (sample 1) was prepared by the slow hydrolysis of double distilled aluminium isopropoxide (*10*) by atmospheric moisture as reported elsewhere (*11*). Fluorided alumina catalysts were prepared by the reaction of alumina with HF solutions (*12*). The fluoride content was determined spectrophotometrically (*13*). Sodium ion-doped catalysts were prepared by impregnation with sodium carbonate solutions as reported elsewhere (*14*). The sodium ion content was estimated by flame photometry (*15*). Alumina and modified alumina catalysts were activated by heating at 100°C for 12 h and further calcination at 600°C for 6 h. High silica faujasite zeolite-Y was prepared by a seed slurry activated crystallization method (*16*). Sodium ions were exchanged with ammonium ions using 5% NH_4Cl solution and the resulting solid was heated at 100°C for 6 h and calcined at 500°C for 3 h to obtain HY-zeolite. Phosphotungstic acid (HPW) was prepared from sodium tungstate and disodium phosphate using the procedure reported elsewhere (*17*). Commercial silicotungstic acid (HSiW) sample (LOBA, India) was used as

[1] To whom correspondence should be addressed.

such. Both HPW and HSiW were activated at 355°C for 3 h. Alumina (sample 8) was prepared by pyrolysis of aluminium isopropoxide as reported in the literature (*11*).

X-ray diffraction studies were performed to characterize all these catalysts and surface area measurements were performed for alumina (216 m^2/g) and modified alumina catalysts (no appreciable change in surface area upon modification). Acidity measurements were performed by the titration of solid catalyst suspended in dry benzene with *n*-butylamine solution using Hammett indicators (*18*). The total acidity of the catalysts was in the order HPW > HSiW > HY-zeolite > F$^-$/Al$_2$O$_3$ > Al$_2$O$_3$ > Na$^+$/Al$_2$O$_3$. When compared to alumina, fluoridation increases the total acidity and also creates stronger acidic sites and sodium ion impregnation lowers the total acidity and also the number of stronger acidic sites.

Apparatus and Experimental Techniques

The catalytic flow reactor and the general experimental technique have been described previously (*19*). Products were analyzed using HPLC (LC5A, Shimadzu, Japan, Zorbax ODS 4.6 mm × 15 cm column, 100% methanol solvent system, spectrophotometric detector) and GLC (CIC, India, FFAP 10% on 60- to 80-mesh Chromosorb G, acid-washed white, 6 ft length, $\frac{1}{8}$ in. diameter column, N$_2$ carrier, FI detector 1 in. = 25.4 mm, 1 ft = 30.5 cm). Identification was made by comparison of retention times with authentic samples and estimation was made by the internal standard method.

RESULTS AND DISCUSSION

Benzyl alcohol, when passed over different oxide catalysts (Al$_2$O$_3$, fluorided Al$_2$O$_3$, HY-zeolite, phosphotungstic acid, and silicotungstic acid) at 300–500°C, has been found to yield anthracene in addition to the normal dehydration product dibenzyl ether and the disproportionation products benzaldehyde, toluene, and water. The results are given in Table 1.

$$PhCH_2OH \xrightarrow[-H_2O]{Al_2O_3} anthracene$$
$$+ PhCH_2OCH_2Ph + PhCHO + PhCH_3$$
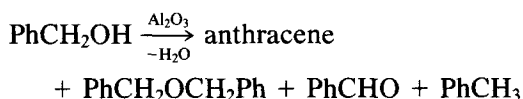
TABLE 1

Reactions of Benzyl Alcohol over Oxide Catalysts at Different Temperatures

| No.	Catalyst	Temperature (°C)	Conversion (%)	Yield (%)[a]				
				Toluene	Benzaldehyde	Anthracene	Dibenzyl ether	Unaccounted[b]
1	η-Al$_2$O$_3$ (sample 1)	300	80	18	17	—	35	10
2	η-Al$_2$O$_3$ (sample 1)	350	93	25	24	12	21	11
3	η-Al$_2$O$_3$ (sample 1)	355	100	29	28	14	17	12
4	η-Al$_2$O$_3$ (sample 1)	380	100	34	33	19	—	14
5	η-Al$_2$O$_3$ (sample 1)	400	100	25	26	34	—	15
6	η-Al$_2$O$_3$ (sample 1)	450	100	15	34	45	—	6
7	η-Al$_2$O$_3$ (sample 1)	500	100	14	37	43	—	6
8	4.75% F$^-$/Al$_2$O$_3$	355	100	20	17	46	Trace	17
9	4.75% F$^-$/Al$_2$O$_3$	400	100	10	8	70	—	12
10	4.75% F$^-$/Al$_2$O$_3$	450	100	8	11	69	—	12
11	4.75% F$^-$/Al$_2$O$_3$	500	100	7	12	63	—	18
12	HY-zeolite	250	59	23	22	Trace	Trace	14
13	HY-zeolite	300	90	33	32	12	—	13
14	HY-zeolite	355	100	18	16	50	—	16
15	HY-zeolite	400	100	10	8	73	—	9
16	HY-zeolite	450	100	9	15	65	—	11
17	HY-zeolite	500	100	8	17	64	—	11
18	HSiW	355	97	25	17	25	7	23
19	HPW	355	96	24	22	33	5	12

Note. Reagent, 5 ml of benzyl alcohol in 15 ml of benzene; catalyst, 5 g; flow rate, 22 ml/h.
[a] Mole percent based on benzyl alcohol taken.
[b] Small amount of PhCH$_2$Ph, PhCH$_2$CH$_2$Ph, and losses.

Toluene and benzaldehyde individually and as a mixture did not yield any anthracene over these catalysts. Benzyl alcohol itself did not yield anthracene in the absence of the catalyst.

When dibenzyl ether was passed over alumina under the reaction conditions, it decomposed completely yielding anthracene as the major product in addition to toluene, benzaldehyde, and water.

$$PhCH_2OCH_2Ph \xrightarrow[450°C]{Al_2O_3} anthracene + PhCH_3$$
$$+ PhCHO + H_2O$$
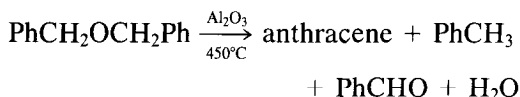
Both benzyl alcohol and dibenzyl ether are known to give, on adsorption over alumina, the same benzyl oxide surface species. o-Benzylbenzyl alcohol (I) formed by the interaction between two such surface alkoxide species is the likely intermediate.
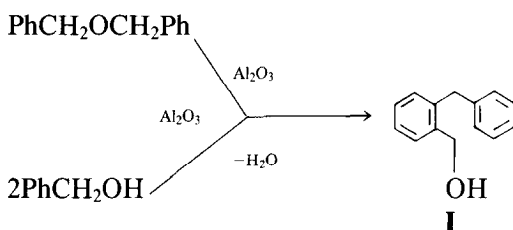
Attempts to isolate this intermediate (I) were unsuccessful but gas chromatographic analysis showed its presence in traces in the product mixture. When the intermediate (I) prepared independently was subjected to the same experimental conditions, anthracene was obtained quantitatively.

On the basis of the above studies, Scheme I is proposed for the formation of anthracene, over alumina. On the more acidic catalysts (HY-zeolite and heteropoly acids) the alkylating species are likely to be benzyl cations rather than benzyl oxides.
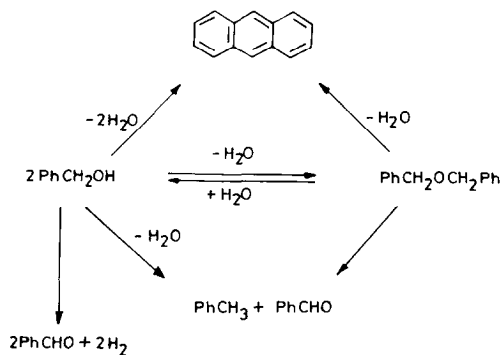
Effect of Temperature on Selectivity

Table 1 gives the results obtained from the reactions of benzyl alcohol over the different catalysts at different temperatures (300–500°C). The product distribution is the result of several competing reactions which are temperature dependent (Scheme II).
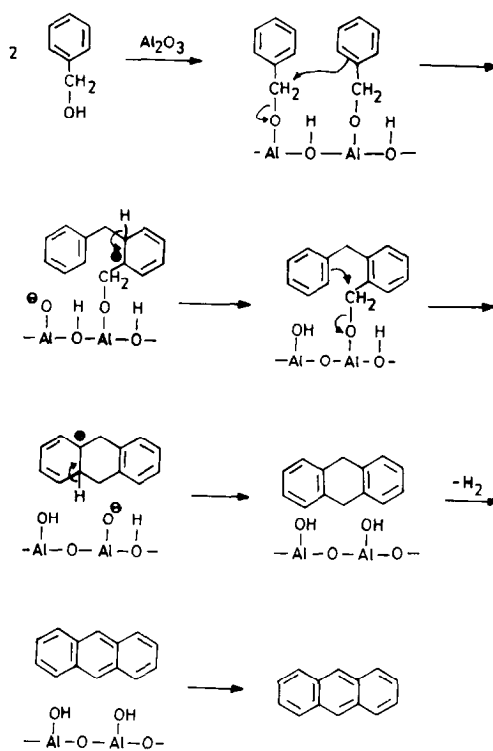
SCHEME I

At low temperature (300°C), over alumina both dehydration to ether and disproportionation to toluene, benzaldehyde and water were found to occur. Anthracene could not be detected at this temperature except on HY-zeolite (No. 13, Table 1). Figure 1 illustrates the variation of the formation of toluene, benzaldehyde, and an-
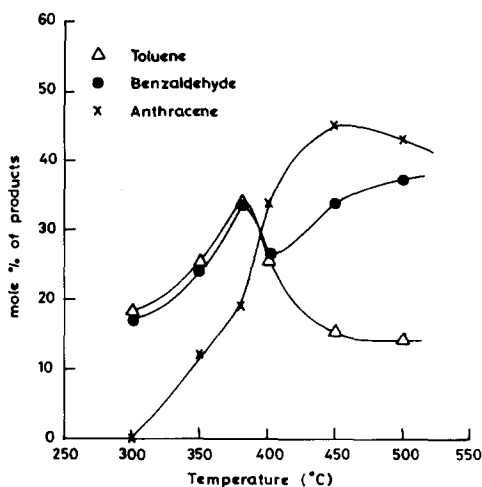
SCHEME II

FIG. 1. Effect of temperature on product distribution.

thracene at different temperatures ranging from 300 to 500°C over alumina.

Toluene and Benzaldehyde

Up to 400°C the ratio of benzaldehyde to toluene in the product mixture is maintained at 1. This is evidently because, as has been reported earlier (1–3), the two are formed in the same primary reaction step, namely disproportionation either from benzyl alcohol or from the ether (Scheme II). The yield of toluene and benzaldehyde increases with temperature and reaches a maximum at about 380°C and then decreases. This is because at higher temperatures, the competing reaction, formation of anthracene, takes over. Above 400°C the ratio of benzaldehyde : toluene is no longer unity but increases due to yet another competing reaction, namely dehydrogenation of benzyl alcohol to benzaldehyde and hydrogen as reported earlier (20). This trend is found on the other catalysts also (Nos. 10 and 11, F⁻/Al₂O₃, and Nos. 16 and 17, HY-zeolite, Table 1).

Anthracene

Anthracene formation involving the alkylation of the aromatic nucleus requires fairly high temperature. It starts around 350°C and reaches a maximum yield around 450°C over alumina. The gradual decrease in its yield above 450°C may be due to the competing dehydrogenation reaction.

Dibenzyl Ether

Dibenzyl ether was detected only at low temperatures. At high temperatures, it undergoes further reactions to give anthracene, toluene, and benzaldehyde.

Role of Acidity of the Catalyst

Among the catalysts listed in Table 1 acidity increases in the order $Al_2O_3 < F^-/Al_2O_3 <$ HY-zeolite $\simeq$ heteropoly acids. It can be seen from Table 1 that at any given temperature selectivity for anthracene formation also increases in that order (Nos. 3, 8, and 14, Table 1) except for the heteropoly acids (Nos. 18 and 19, Table 1). The heteropoly acids are less porous solids of much lower surface area than Al_2O_3 or the zeolite. It is possible that the texture of the catalyst may also play a role in the selectivity. Alumina, fluorided alumina, and HY-zeolite contain both Brønsted and Lewis acidic sites but heteropoly acids are known to be Brønsted acids. The formation of anthracene may require both Brønsted and Lewis acid sites which may also be a reason for the lower yield of anthracene over heteropoly acids. To verify the role of acidity on selectivity further, alumina catalysts impregnated with sodium ions (Nos. 4–7, Table 2) and a relatively low acidic alumina (11) obtained by the pyrolysis of aluminium isopropoxide (No. 8, Table 2) were prepared and used for the benzyl alcohol reactions (see Table 2).

From Table 2, it is clear that ether formation is favored by sodium ion-doped alumina catalysts containing weak acidic sites (samples 4–7) and the disproportionation is favored by fairly acidic pure alumina catalyst (sample 1). The result obtained in the case of sample 8 (11), a weakly acidic catalyst, corroborates this conclusion.

The fluorided catalysts (samples 2 and 3)

TABLE 2

Reaction of Benzyl Alcohol over Alumina and Modified Alumina Catalysts at 380°C

No.	Catalyst	Conversion (%)	Yield (%)[a]				
			Toluene	Benzaldehyde	Anthracene	Dibenzyl ether	Unaccounted
1	η-Al_2O_3 (sample 1)	100	34	33	19	—	14
2	2.11% F^-/Al_2O_3	100	20	19	53	—	8
3	4.75% F^-/Al_2O_3	100	16	16	61	—	5
4	0.25% Na^+/Al_2O_3	100	33	32	17	1	17
5	0.50% Na^+/Al_2O_3	100	31	30	14	7	18
6	1.00% Na^+/Al_2O_3	95	27	26	11	14	17
7	1.50% Na^+/Al_2O_3	81	15	13	5	31	17
8	Al_2O_3 (sample 8)	88	15	16	7	37	13

Note. Reagent, 5 ml of benzyl alcohol in 15 ml of benzene; catalyst, 5 g; flow rate, 22 ml/h.
[a] Refer to footnotes *a* and *b* of Table 1.

are more selective for anthracene formation than for disproportionation suggesting that increased acidity favors the former reaction, as discussed already. Figure 2 shows the influence of sodium ions on different reactions of benzyl alcohol over alumina. The formation of anthracene, toluene, and benzaldehyde decreased as the amount of sodium ion increased, while ether formation increased. Increasing the Na^+ content decreases the acidity of alumina. The shift in selectivity shows that both disproportionation and anthracene formation are reactions which require relatively stronger acidity than ether formation.

FIG. 2. Effect of sodium ion content of alumina on product distribution.

Substituted Benzyl Alcohols

Benzyl alcohols substituted in the side chain and in the nucleus were included in the present investigation. In the case of benzhydrol, only the disproportionation reaction was found to occur to yield benzophenone, diphenylmethane, and water over alumina as already reported (20).

$$\overset{\displaystyle OH}{\underset{\displaystyle |}{Ph-CH-Ph}} \xrightarrow[400°C]{Al_2O_3} PhCOPh + PhCH_2Ph$$

$$+ H_2O$$

When 1-phenylethanol was passed over alumina at 400°C, the dehydration product, styrene, was obtained in a major amount in addition to the disproportionation products namely acetophenone and ethylbenzene. The expected 9,10-dimethylanthracene was not detected. Reactions of 2-, 3-, and 4-methylbenzyl alcohols over alumina yielded in each case a mixture of hydrocarbon derivatives in addition to the ether and disproportionation products. The ^1H NMR of the solid mixture showed the presence of a methyl group but the efforts to separate the individual compounds from the mixture by column chromatography were not successful. At high temperatures, demethyl-

ation was also noted, which further increased the complexity of the mixture.

Synthetic Utility

Reactions of benzyl alcohol over HY-zeolite have been optimized to form a convenient method for preparing pure anthracene. A solution of 0.2 mol of benzyl alcohol (21.6 g) in benzene (diluted to 50 ml) was passed over a bed of HY-zeolite (10 g) at a rate of 22 ml/h at 400°C. The products were collected in a water-cooled condenser. After being dried over anhydrous Na_2SO_4, the solvent was evaporated. A viscous liquid was obtained. Addition of a small amount of hexane to it yielded solid product. The solid anthracene was filtered from the reaction product mixture and recrystallized from hot hexane. The yield was 11.5 g (64.5% based on benzyl alcohol) (mp = 216°C).

CONCLUSIONS

The results of our study of the reaction of benzyl alcohol over oxide catalysts under different experimental conditions led us to the following conclusions:

1. Dibenzyl ether is formed over weakly acidic catalysts (Na^+-doped alumina and alumina prepared by pyrolysis of aluminium isopropoxide) at low temperature (300°C).

2. Disproportionation of benzyl alcohol and decomposition of dibenzyl ether to toluene, benzaldehyde, and water are facilitated by fairly acidic catalysts (pure alumina) at moderately high temperature (380°C).

3. Anthracene formation is favored over highly acidic catalysts (fluorided alumina and HY-zeolite) at higher temperatures (>400°C).

4. At temperatures above 400°C, a fourth competing reaction, dehydrogenation of benzyl alcohol to benzaldehyde occurs.

REFERENCES

1. Jayamani, M., and Pillai, C. N., *J. Catal.* **82,** 485 (1983).
2. Jayamani, M., Murugesan, N., and Pillai, C. N., *J. Catal.* **85,** 527 (1984).
3. Ananthan, S., Ganesan, K., and Pillai, C. N., *Indian J. Chem.* **26A,** 512 (1987).
4. Ungnade, H. E., and Crandall, E. W., *J. Amer. Chem. Soc.* **71,** 3009 (1949).
5. Ungnade, H. E., and Crandell, E. W., *J. Amer. Chem. Soc.* **71,** 2209 (1949).
6. Kaeding, W. W., *J. Catal.* **95,** 112 (1985).
7. Cavallaro, S., Pino, L., Tsiakaras, P., Giordano, N., and Rao, B. S., *Zeolites* **7,** 408 (1987).
8. Tarama, K., Yoshida, S., Katayama, Y., and Bitoh, T., *J. Japan Pet. Inst.* **11,** 771, 775 (1968).
9. Yashima, T., Ahmad, H., Yamazaki, K., Katsura, M., and Hara, N., *J. Catal.* **16,** 273 (1970); **17,** 151 (1970).
10. Vogel, A. I., "A Textbook of Practical Organic Chemistry," 3rd ed., p. 320. Longmans, Green, London, 1956.
11. Jayamani, M., Viswanathan, B., and Pillai, C. N., *J. Catal.* **89,** 560 (1984).
12. Scokart, P. O., Selim, S. A., Damon, J. P., and Rouxhet, P. G., *J. Colloid Interface Sci.* **70,** 209 (1979).
13. Boltz, D. F., and Howell, J. A., "Colorimetric Determination of Non-metals," 2nd ed., p. 118. Wiley, New York, 1978.
14. Ramana, D. V., and Pillai, C. N., *Canad. J. Chem.* **47,** 3705 (1969).
15. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis," 3rd ed., p. 879. Longmans, Green, London, 1969.
16. Kerr, G. T., *Catal. Rev. Sci. Eng.* **23,** 281 (1981).
17. Bailor, J. C., in "Inorganic Synthesis" (H. C. Booth, Ed.), Vol. 1, p. 132. McGraw–Hill, New York, 1939.
18. Benesi, H. A., *J. Amer. Chem. Soc.* **78,** 5490 (1956).
19. Jayamani, M., and Pillai, C. N., *Synth. Commun.* **15,** 535 (1985).
20. Unni, M. P. K., Santhanagopalan, S., and Pillai, C. N., *J. Indian Chem. Soc.* **1,** 582 (1973).