Studies in Catalytic Reactions of Carbons: Part VII—Catalytic Chlorination of Toluene in Presence of Active Carbons

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Toluene vapours, mixed with chlorine gas, when led over an active carbon bed, maintained at elevated temperatures, get converted substantially into benzyl chloride. The optimum temperature for the reaction lies in 250-400° range. The catalytic performance of a carbon at its optimum temperature varies not so much with surface area as with surface unsaturation. Catalytic activity can be enhanced by generation of additional unsaturated sites by suitable treatments. The reaction appears to proceed through dissociative chemisorption of chlorine at the unsaturated and other active sites and interaction of toluene vapour with some of the chlorine atoms released from the surface under the sweeping action of the gas at elevated temperatures. As the surface gets increasingly blocked by chemisorbed chlorine, the catalytic efficiency falls but can be revived on desorption of chlorine by treatment in a current of hydrogen at 500°.

SEVERAL workers have investigated chlorination of organic compounds[1-3] including toluene[4-6] in the presence of different catalysts or under γ-rays and other irradiations[5,6]. Puri and Bansal[7] while studying chemisorption of chlorine by charcoals and carbon blacks reported that if toluene vapours mixed with chlorine are led over the carbon bed there is a partial halogenation of toluene. However, no attempt was made to investigate the reaction in detail. In view of the industrial importance of chlorinated products of toluene particularly of benzyl chloride, it was thought of interest to study the reaction in some details with a view to getting an insight into the mechanism of the reaction. The results of such a study are reported in this paper.

Materials and Methods

Five samples of active carbons, designated as A, B, C, D and E, marketed by different manufacturers were used. The oxygen and hydrogen contents obtained by ultimate (micro) analysis, specific surface areas as calculated from adsorption isotherms (273 K) of carbon dioxide by applying Dubinin-Polanyi equation[8-10], and surface unsaturations obtained from the amounts of bromine chemisorbed on treatment with aqueous bromine[11] are recorded in Table 1. Toluene used was of chemically pure (BDH). Chlorine gas was prepared in the laboratory freed of acidic and other impurities and then dried in the usual way.

Procedure — Chlorine gas was passed through a flask containing a known amount (usually 0·47 mol) of toluene kept close to its boiling point under reflux in an oil-bath. The gas mixed with toluene vapour was led over a carbon bed (usually 3 g) held in the form of a plug in a slanting pyrex glass tube (2·3 cm in diam.) heated to different temperatures in an electric furnace. The rate of passage of the gaseous mixture was so adjusted by applying

TABLE 1 — A FEW CHARACTERISTICS OF ACTIVE CARBONS USED

Active carbon	Surface area (m^2/g)	Surface unsaturation (millieq/100 g)	Hydrogen content (g/100 g)	Oxygen content (g/100 g)
A	1122	123	2·75	3·66
B	1046	155	2·61	3·36
C	832	139	2·57	4·12
D	922	83	2·86	3·94
E	549	125	1·94	2·08

suction at the other end that the entire amount of toluene was led over the bed within a certain specified period of time. The outcoming gas consisting essentially of unreacted chlorine and toluene together with chlorinated products and hydrogen chloride formed, if any, was led into a series of flasks provided with water condensers where toluene and chlorinated products were collected as condensate while chlorine and hydrochloric acid were dissolved in water. In order to estimate HCl in the solution, chlorine was first eliminated by adding excess KI and titrating against sodium thiosulphate in the usual manner. The same solution was then titrated against standard NaOH using phenolphthalein as the indicator. The condensate was checked by TLC and, besides toluene, only one halogenated product was detected. This was identified (b.p., UV and NMR) as benzyl chloride. Benzyl chloride, on account of its much higher boiling point (179°C), could easily be separated from toluene by fractional distillation.

Results and Discussion

It was found in a few preliminary experiments, using carbon (A) as a catalyst bed, that the conversion of toluene into benzyl chloride took place

to a negligible extent below 200°C but to an appreciable extent between 250° and 400°C. There was no such conversion in the absence of any carbon. The extent of the reaction was found to increase with the weight of the carbon bed used as the catalyst, although the amount of conversion per g carbon decreased on increasing the weight of the carbon bed beyond 3 g. In most of the experiments, therefore, the weight of the carbon bed was fixed as 3 g.

The results obtained on passing toluene vapour (0·47 mol) mixed with chlorine over 3 g carbon bed heated to 250°, 300° and 400°C are recorded in Table 2. It is seen that the optimum temperature for maximum conversion of toluene into benzyl chloride varies from carbon to carbon. Thus while it is 250° for carbon (B), 300° for carbons (A), (C) and (D), it is 400° for carbon (E). These carbons have recently been characterized by estimating the relative abundance of their micropores[12]. It has been found that the relative abundance of micropores increases, broadly, in the order: $B \approx A < C \approx D < E$. Since diffusion of gases through micropores is a highly activated process, it is evident that the temperature required for effective diffusion of reacting gases through the porous network of these materials, so as to come into contact with the internal surface and active sites located within, should be in the same increasing order as mentioned above. According to this view, the optimum temperature for maximum reaction should be highest for carbon (E), comparatively lower for (C) and (D) and lowest for (A) and (B). This is amply borne out by the observations recorded in Table 2, except for the fact that the optimum temperature in the case of (A) should also have been 250° as for (B), and not 300° as actually observed. This may be due to differences in the size-distribution of pores within the micropore range itself, in the case of (A) and (B). These observations, in any case, indicate the role of porosity and pore-size distribution as important factors in determining catalytic efficiencies of adsorbent carbons for gaseous reactions. The fall in catalytic activity of a carbon beyond the optimum temperature in each case may be due to fall in their tendency to chemisorb chlorine at higher temperatures[13]. The amount of HCl formed is seen to be invariably in excess of that of benzyl chloride formed. This may be due to interaction of chlorine with hydrogen contained in the carbons during the halogenation process and also possible hydrolysis of chlorine in water to a small extent during the estimation.

The effect of increasing the time period of passage of the same amount of chlorine over the catalyst; i.e. from 1 hr to 2, 3 hr etc. was also studied. The carbon bed was maintained at 300° in the case of (A), (B), (C) and (D) and at 400° in the case of (E). The values for percentage conversions of toluene into benzyl chloride, determined as before, are included in Table 2. It is observed that the percentage conversion of toluene into benzyl chloride in the presence of each carbon sample rises considerably if the gas passage takes 2 hr. A further increase, though smaller in magnitude, is also observed if the passage of gas takes 3 hr.

TABLE 2 — PERCENTAGE CONVERSION OF TOLUENE INTO BENZYL CHLORIDE ON CARBON BEDS MAINTAINED AT DIFFERENT TEMPERATURES

(Carbon bed, 3 g; time of passage = 1 hr; amount of toluene used = 0·47 mol)

Carbon sample	Benzyl-chloride formed (mol)	Conversion %			HCl (mol)
BED MAINTAINED AT 250°C					
A	0·048	10·2	—	—	—	0·118
B	0·166	35·3	—	—	—	0·280
C	0·020	4·3	—	—	—	0·105
D	0·086	18·3	—	—	—	0·182
E	0·019	4·0	—	—	—	0·091
BED MAINTAINED AT 300°C					
A	0·111	23·6 (44·5)*	(46·8)†	(51·6)‡	0·189
B	0·096	20·4 (37·3)*	(41·9)†	(49·7)‡	0·185
C	0·092	19·6 (36·2)*	(40·2)†	(45·6)‡	0·192
D	0·104	22·1 (33·3)*	(36·4)†	(38·8)‡	0·190
E	0·066	14·1 —	—	—	0·125
BED MAINTAINED AT 400°C					
A	0·072	15·3	—	—	—	0·124
B	0·042	8·9	—	—	—	0·088
C	0·042	8·9	—	—	—	0·090
D	0·050	10·6	—	—	—	0·098
E	0·225	47·9 (67·4)*	(68·1)†	(70·4)‡	0·380

*Passage of the same amount of toluene for 2 hr.
†Passage of the same amount of toluene for 3 hr.
‡Passage of the same amount of toluene for 3 hr but the diam. of the reaction tube was 1·4 cm instead of 2·3 cm in other experiments.

In another set of experiments, the length of the 3 g carbon bed was increased by reducing the diameter of the reaction tube from 2·3 cm to 1·4 cm while allowing 3 hr time for the passage of the gas. The performance of each carbon was found to rise further as shown by the data in Table 2. It is interesting to note that nearly 50% of toluene can be converted into the product in the catalytic presence of (A) and (B) at 300° and nearly 70% in the presence of active carbon (E) at 400°, thereby proving the effectiveness of carbon catalyst for this reaction.

There is need, however, to understand the mechanism of the catalytic performance of carbons for this reaction. Puri and Bansal[7] while working on chemisorption of chlorine by charcoals and carbon blacks at elevated temperatures indicated possibility of formation of chlorine atoms through interaction of the gas with hydrogen atoms released from the carbon (cf. $H + Cl_2 \rightarrow HCl + Cl$). If halogenation of toluene is due to the activity of chlorine atoms so produced, the amount of benzyl chloride formed cannot, in any case, be more than the hydrogen content (cf. Table 1) of the carbon used. Actually the amount of benzyl chloride obtained is seen to be much more than that.

Further, it was also of interest to check if the same carbon bed could be used for subsequent runs as well. The results of these experiments, given

TABLE 3 — CONVERSION OF TOLUENE INTO
BENZYL CHLORIDE DURING SUCCESSIVE RUNS OVER THE
SAME CARBON BED MAINTAINED AT
300° AND AFTER REGENERATION OF THE CATALYST

(Time of passage = 3 hr; amount of toluene = 0·47 mol)

Carbon used	Conversion (%) after successive runs			Conversion (%) on regenerated carbons
	First	Second	Third	
A	46·8	38·5	11·4	42·2
B	41·9	30·4	10·1	39·6
C	40·2	26·0	8·4	42·7
D	36·4	21·6	9·7	37·8
E	68·1*	34·3*	8·6*	63·5*

*Conversion at 400° which is the optimum temperature for this carbon.

in Table 3, show that catalytic efficiency of each carbon suffers a substantial fall at each successive run. This may be due to chemisorption of chlorine during the reaction thereby blocking some of the active sites besides an appreciable fraction of the surface.

This view was checked in two ways: firstly by estimating surface unsaturation of each carbon after it had been used in three successive runs and secondly by heating the same in a current of hydrogen at 500°C for 3 hr. It was found that surface unsaturation of each carbon which was appreciable in the beginning (cf. Table 1) had fallen almost to zero after the third run, confirming the blockage of the unsaturated sites. The heat-treatment in hydrogen, in the second set of experiments, was found to result in the liberation of appreciable amounts of HCl gas indicating desorption of chlorine which, obviously, must have been chemisorbed on the carbon surface during the reaction. Toluene was not detected during the desorption process. With the desorption of chlorine in this manner, the catalytic efficiency of each carbon was found to be almost fully restored or even slightly enhanced as shown by the data in Table 3.

These results not only provide sufficient evidence to show that the sites involved in the catalytic

chlorination of toluene are the same which are also involved in chemisorption of chlorine at about the same temperature range, viz. 300-400°C (ref. 7) but also provide a method of regenerating the carbon catalyst. The catalytic functioning of an activated carbon, in fact, appears to lie in its capacity to chemisorb chlorine. The toluene vapour led over such a surface may then interact with some of the chlorine atoms which might be released from the surface, under the sweeping action of the gaseous stream at elevated temperatures, yielding benzyl chloride. It has been shown before[13] that there is a certain optimum temperature (300-400°C) for maximum chemisorption of chlorine, which varies with the nature of carbon. It has been observed in the present study that there is a certain optimum temperature (300-400°C) for maximum catalytic performance of active carbons.

The catalytic performance of a carbon, as revealed by the percentage conversion of toluene into benzyl chloride at the optimum temperature does not appear to be closely related to its specific surface area. In fact, carbon (E) having lowest surface area shows maximum catalytic activity at the optimum temperature of 400°. It appears that other factors such as pore structure, as already mentioned, and surface unsaturation are also involved. In order to check the influence of unsaturated sites more directly, an attempt was made to enhance surface unsaturation of the various carbons by giving them oxidation treatment either with (i) aqueous potassium persulphate or (ii) aqueous hydrogen peroxide and then evacuating them at temperatures around 800°C (ref. 11). The results of these experiments are given in Table 4. It is interesting to note that with the development of additional unsaturated sites, catalytic performance of each carbon increases considerably even though surface area increases significantly only in the case of carbon (E). These treatments, incidentally, place at our disposal effective methods for enhancing catalytic activities of adsorbent carbons for this reaction.

Walker and coworkers[14,15] were able to generate "active surface area" (defined as the area occupied by the oxygen chemisorbed, on exposure to the gas at 350°C under low oxygen pressure of 0·5 torr) in graphitized carbon black by giving them diffe-

TABLE 4 — EFFECT OF INCREASING SURFACE UNSATURATION ON CATALYTIC PERFORMANCE OF ACTIVE CARBONS

(0·47 mol toluene vapour mixed with chlorine and passed for 3 hr on various carbon beds maintained at 300° or 400°C)

Carbon used	Surface area (m²/g)			Surface unsaturation (millieq./100 g)			Conversion (%)		
	Before treatment	After treatment		Before treatment	After treatment		Before treatment	After treatment	
		(i)	(ii)		(i)	(ii)		(i)	(ii)
A	1122	1161	1258	123	435	451	46·8	56·7	52·6
B	1046	1230	1174	155	365	344	41·9	48·8	45·9
C	832	988	1023	139	401	320	40·2	50·1	48·4
D	922	1059	1011	83	308	331	36·4	49·0	47·5
E	549	692	724	125	243	251	68·1*	79·9*	76·9*

(i) Treatment with pottassium persulphate followed by evacuation at 800°C.
(ii) Treatment with aqueous hydrogen peroxide followed by evacuation at 800°C.
*Conversion at 400° which is the optimum temperature for the carbon.

TABLE 5 — EFFECT OF CAUSING DIFFERENT BURN-OFFS TO ACTIVE CARBON (A) ON ITS CATALYTIC PERFORMANCE

[Time of passage of toluene (0·47 mol) = 3 hr; carbon maintained at 300°]

Burn-off (%)	Surface area (m²/g)	Surface unsaturation (millieq./100 g)	Conversion (%)
nil	1122	123	46·8
2·5	1258	488	56·0
5·96	1380	538	62·4
9·81	1479	576	77·1

rent burn-offs in oxygen at 625° at low pressures. Puri *et al.*[16] have shown that a part of the active area generated in charcoals and carbon blacks in this manner corresponds to generation of new unsaturated sites. The results of study on the effect of giving different burn-offs up to 10% to one of the active carbons on surface area, surface unsaturation and catalytic performance are presented in Table 5. It is seen that both surface area and surface unsaturation increase at each successive burn-off; the maximum increase in the former value is about 36% while that in the latter it is over 500%. The catalytic performance is also observed to increase at each burn-off and the percentage conversion of toluene goes up from about 47% to nearly 77% after burn-off of 10%. This places at our disposal another method of activating carbons for the catalytic chlorination of toluene.

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