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REGIOSELECTIVE *PARA*-CHLORINATION OF ALKYLBENZENES ON CHEMICALLY-MODIFIED SILICA SURFACES

Hisatoshi KONISHI, Kiyoshi YOKOTA, Yuji ICHIHASHI, Tamon OKANO,
and Jitsuo KIJI
Department of Environmental Chemistry and Technology
Faculty of Engineering, Tottori University, Tottori 680

Chlorination of alkylbenzenes was carried out with chlorine in carbon tetrachloride in the presence of chemically-modified silica catalysts. The *para*/*ortho* ratios were remarkably higher than those obtained in the $FeCl_3$-catalyzed chlorination. *t*-Butylbenzene was chlorinated at *para*-position almost exclusively. The catalyst could be reused several times.

The reaction of adsorbed organic substrates on silica and suitable solid supports have been studied with current interest,$^{1)}$ especially in the regioselective functionalization of aliphatic C-H bonds.$^{2-5)}$ Although a few studies have been reported$^{6-9)}$ on the use of silica as a catalyst for electrophilic aromatic substitution, little attention has been paid to the regioselectivity of the reactions. The *para*/*ortho* ratios in the silica catalyzed halogenations of alkylbenzenes are higher than those of the conventional procedures.$^{7)}$ The relatively high isomer ratios of *para*/*ortho* indicate that the *ortho*-positions are more sterically hindered to the attack of activated electrophile on the silica surface. It is expected that the isomer ratio might be further improved by directing the orientation of the substrate on the surface. Thus, we have used chemically-modified silica surface in the hope that the substrates would favorably be oriented as shown in Figure 1. We now report the chlorination of alkylbenzenes on chemically-modified silica surfaces.

Silica-1, (Wakogel C-200, for column chromatography),$^{10)}$ was chemically-modified as shown in Scheme 1. The amount of the anchored benzamide moieties in silica-3 was determined to be 0.80 meq/g by elemental analysis for nitrogen.

$$\underset{(1)}{[SiO_2]} \xrightarrow{\text{i}} \underset{(2)}{[SiO_2]{\equiv}Si(CH_2)_3NH_2} \xrightarrow{\text{ii}} \underset{(3)}{[SiO_2]{\equiv}Si(CH_2)_3NHCOAr}$$

i. 3-Aminopropyltriethoxysilane, PhH, Δ
ii. 3,5-Dinitrobenzoyl chloride, base, PhH, r. t.

Scheme 1. Preparation of Chemically-Modified Silica

Table 1. Chlorination of Cumene Using Silica Catalysts

Run	Silica	Additive	Conv. (%)[d)]	p/o ratio
1	(1)		90.4	1.17
2	(2)		78.5	1.57
3	(1)	amide[b)]	86.4	1.27
4	(3)		59.3	3.86
5	(3)	K_2CO_3[c)]	56.9	4.28
6	(3a)		50.1	4.06
7	(3a)	K_2CO_3[c)]	51.0	5.09
8	(3)[a)]		72.6	3.53

a) Reused catalyst. b) N-Propyl-3,5-dinitrobenzamide, 1 mmol.
c) 1.00 g. d) Total yields of p- and o-chlorocumenes.

A typical run is as follows; to a mixture of cumene (600 mg, 5 mmol) and a catalyst (1.00 g) was added a solution of chlorine (5 mmol in 20 ml of carbon tetrachloride) with magnetic stirring at 30 °C. After 1 h stirring, the catalyst was filtered off and washed with dichloromethane. The filtrate was washed with water, dried, and subjected to gas chromatographic analysis. The chlorinated products were o- and p-chlorocumenes, and no dichloro derivative was observed. Even in the presence of light , chlorination of the isopropyl group occurred to an extent of less than 0.3%. The regioselectivity for the reaction was expressed as the para/ortho ratio (p/o). The results of the chlorination of cumene using silica catalysts are summarized in Table 1.

In the absence of silica, no chlorinated product was observed. Compared with $FeCl_3$ catalysis (p/o 0.69),[12)] silica-1 catalysis showed a higher selectivity (run 1). These results were similar to those reported by Yaroslavsky.[7)] N-Propyl-3,5-dinitrobenzamide itself had no catalytic activity for the chlorination reaction.[13)] And also, the p/o selectivity of silica-1 catalysis was not appreciably affected by the addition of the amide (run 3). However, the p/o ratio was markedly increased by using silica-3 (run 4). Therefore, it seems that the anchoring groups on the surface would play an important role in increasing the regioselectivity of the reaction.

The selective para-chlorination of cumene may be explained as shown in Figure 1. After the anchoring reaction of triethoxysilyl groups with silica, not a few silanol groups still remain on the silica surface.[14)] Chlorine molecules on the surface are activated with silanol groups,[6)] while chlorine molecules in the solution are not activated. The alkylene chains of the anchored amide are probably directed away from the surface and aligned parallel to each other. The benzamide moieties interact with aromatic nuclei of cumene by charge-transfer force and/or steric repulsion. Thus, the alkylbenzene is oriented in a definite pattern. The para-position of alkylbenzene is accessible to the activated chlorine, and para-chlorination occurs on silica-3 surface.

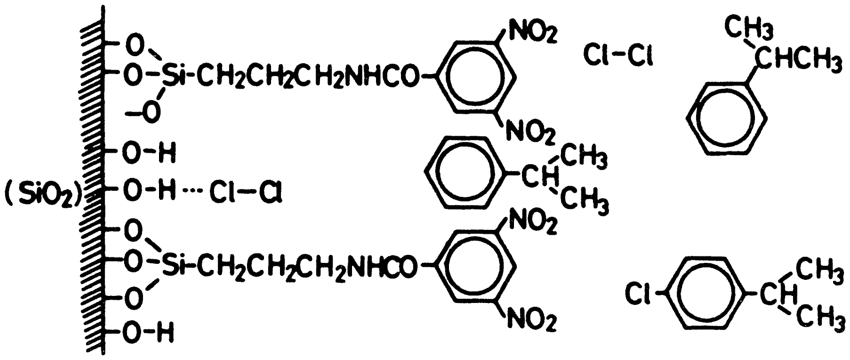

Figure 1. Schematic Representation of Cumene Molecules on the Modified Silica Surface in Solution. The reacting benzene ring is parallel to and above the dinitrobenzoyl moieties.

There is a strong influence of the structure of the anchored groups on the p/o ratios. The reaction of silica-2 with 2,4-dinitrochlorobenzene, 4-nitrobenzoyl chloride, and 3-nitrobenzoyl chloride gave the corresponding chemically-modified silicas. The chlorination of cumene was carried out using these silicas under the same experimental conditions. The p/o ratios were 1.57, 2.24 and 1.76, respectively. This supports the idea that the selectivity is governed by the electrostatic and/or steric influences of the anchoring groups on the surface.

The p/o ratio was improved by adding an excess of potassium carbonate, which removes hydrogen chloride liberated during the reaction.

Chemically-modified silica catalysts prepared from non-porous Aerosil 300[15)] (silica-3a) gave somewhat better results than the catalysts prepared from Wakogel C-200. The best result, p/o ratio 5.09, was obtained with silica-3a in the presence of potassium carbonate.

The recovered catalysts could be used several times after drying under vacuum. The reused catalyst showed slightly lower selectivity than the original one, and was more reactive. This may be due to the increase in surface area, since the silica was ground with magnetic stirring during the reaction.

Using silica-3 and potassium carbonate, some alkylbenzenes were also chlorinated regioselectively. The observed p/o ratios were 2.22 for ethylbenzene, 3.00 for pentylbenzene, and >55 for t-butylbenzene, and were distinctly higher than those with $FeCl_3$ catalysis (p/o 0.44, 0.54, and 7.93, respectively).[12)]

The selectivity of the reaction appears to be dependent on the structures and the amount of the anchored groups, and the fine structure of the silica surface. Extensive work on the utilization of the chemically-modified silica surface as reaction media is now under way.

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10) Wakogel C-200, Wako Pure Chemicals, was purified by refluxing in concd. HCl for 4 h, washed until neutral with distilled water, and dried in a vacuum desicator to a constant weight.11)
11) J. S. Fritz, J. N. King, Anal. Chem., 48, 570 (1976).
12) Ferric chloride (90 mg) was used in place of silica.
13) Cumene (5 mmol), chlorine (5 mmol), and N-propyl-3,5-dinitrobenzamide (1 mmol) were stirred in carbon tetrachloride (20 ml) at 30 °C for 12 h. The reaction flask was covered with opaque material to exclude light.
14) L. L. Murrel, "Advanced Materials in Catalysis," ed. by J. J. Burton, R. L. Garten, Academic Press, New York (1977), Chap. VIII.
15) Aerosil 300 was kindly supplied from Nippon Aerosil in the form of powder, typically 8 nm in diameter. It had a specific surface area of 300±30 m^2g^{-1} (manufacturer's determination).

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