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Friedel-Crafts Reaction in the Heterogeneous System

VI. A Friedel-Crafts Isopropylation of Toluene with Isopropyl Halides Catalyzed by Calcined Iron Sulfates. Substrate and Positional Selectivity

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The Friedel-Crafts isopropylation of toluene with isopropyl halides catalyzed by iron sulfates heat-treated in air at high temperature was carried out at 150°C in the gas–solid system using a flow system. The maximum activity (total conversion: 19 mole%) was shown over the catalyst calcined at 700°C. The mixture of products was quite clear, and the isomer distributions were almost the same over all the catalysts and also remained constant during run. The isomers were 35–38% *ortho*-, 24–26% *meta*- and 39–40% *para*-isopropyltoluene. The relative rate of toluene to benzene, k_T/k_B, in the present gas phase system where the contact time is quite short was obtained to be 2.21, which is in relatively good agreements with Olah and co-worker's [*J. Amer. Chem. Soc.* **86**, 1046 (1964); **87**, 5788 (1965)] and Brown and Smoot's [*J. Amer. Chem. Soc.* **78**, 6255 (1956)] values, but not in agreement with the recent report by Nakane and co-workers [*J. Org. Chem.* **36**, 2753 (1971)]. From these values, the positional reactivities of toluene, o_f, m_f, p_f, were estimated to be 2.39, 1.54 and 5.37, respectively.

INTRODUCTION

The Friedel-Crafts reaction, which is one of the most studied organic reactions, is known to proceed over Lewis-type catalysts such as $AlCl_3$ and $GaBr_3$, and this type of catalyst has been most used (*1*). It has been recently found that ferrous and ferric sulfates calcined in air showed high catalytic activity and selectivity for the benzylation of toluene with benzyl chloride in comparison with those of other solid acids such as Al_2O_3 and $NiSO_4$ (*2–4*). Both iron sulfates calcined at 700°C also showed the highest activity for benzylation and benzoylation of toluene with benzyl chloride and benzoyl chloride, respectively (*5*). In order to know the properties of these new catalysts, the present work was undertaken to study the isopropylation of toluene with isopropyl halides over these catalysts in gaseous phase using a conventional flow system.

EXPERIMENTAL METHODS

Toluene and benzene, guaranteed reagents (GR), were purified by distillation over sodium metal. Isopropyl halides which are high purity commercially available were used without further purification. Catalysts were prepared as follows: iron sulfates [$FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$] (GR) were heated at 150°C in air for 1 hr, and powdered to 100–200 mesh size, and then they were calcined in a pyrex or quartz glass tubing at various temperatures ranging from 600 to 900°C in air for 3 hr. Thus prepared catalysts were kept in sealed glass tubings until use. The reaction was carried

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TABLE 1

Catalytic Activity and Selectivity for Isopropylation of Toluene with Isopropyl Bromide at 150°C

Catalyst	Calcination temp (°C)	Conversion[a] (mole%)	Isopropyltoluene (%)[b]		
			ortho-	*meta-*	*para-*
$Fe_2(SO_4)_3$	600	2.5			
	700	19.0	35.9(36.6)	23.7(23.3)	40.4(40.1)
	800	17.0			
	900	15.3	34.8(33.3)	25.8(25.5)	39.4(41.2)
$FeSO_4$	700	19.0	37.7(36.1)	23.6(23.3)	38.7(40.5)

[a] Between 40 and 50 min in the reaction time.

[b] Observations with 0–10 min in the reaction time. Numerals in parentheses correspond to those from 40 to 50 min in the reaction time.

out at 150°C in a flow system using a highly purified nitrogen as a carrier gas. A vaporized mixture of toluene and isopropyl bromide in the equimolar ratio and nitrogen were passed through the catalyst bed (1 g catalyst used). The flow rates of the mixture and nitrogen were 5.4 ml/hr (as liquid) and 15 ml/min (STP), respectively. The catalyst was heat-treated in the reactor at 400°C for 1.5 hr before the run. In order to know the total conversion, the products were collected for 10 min intervals in a trap cooled with ice bath and then they were analyzed by a gas chromatograph with flame ionization detector (FID) using a 2 m column of PEG 1000 on Flusin T (at 80°C, N_2:0.8 kg/cm^2). The total conversion was defined as the amount of toluene converted to the product in molar percent unit. The separation of *o*-, *m*-, *p*-isopropyltoluene was performed by a 45 m capillary column of Ucon LB-550-X(100°C; N_2:1.2 kg/cm^2). The relative rate of toluene and benzene was obtained by the competitive reaction of these aromatics (1:1 molar ratio) with the equimolar amount of isopropyl bromide by the same method as described above.

RESULTS AND DISCUSSION

Figure 1 shows the time-course of the reaction. Both ferric and ferrous sulfates calcined at 700°C kept their catalytic activity constant during the reaction, whereas the catalyst heat-treated at 600°C lost its activity immediately after the reaction. On the other hand, the catalyst heat-treated at 800°C showed gradual increase of its activity. The reason for the increase or decrease of the activity depending on calcination temperature is not clear at present.

Table 1 summarizes the activity of ferric sulfates calcined at various temperatures and of ferrous sulfates calcined at 700°C, together with the product distributions. As observed in the benzylation and benzoylation reactions (*5*), the maximum activity was shown over the catalyst calcined at 700°C for ferric sulfate. The same behavior of the ferrous sulfate may be expected.[1] The conversions were not decreased so much with the higher calcination temperatures above 700°C, whereas they were decreased with benzylation and benzoylation reactions.

The mixture of product was quite clear

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[1] The total conversions for the isopropylation of toluene with isopropyl chloride and with isopropyl iodide over $Fe_2(SO_4)_3$ (calcined at 700°C) at 150°C were 11.0 and 5.5 mole%, respectively, between 40 and 50 min. Those with isopropyl bromide over $FeSO_4$ (700°C) at 200 and 250°C were 12.0 and 5.0 mole%, respectively, during the final period of reaction.

in all runs and any products other than listed in the table were not observed in glc. The product distributions were almost the same over all the catalysts used and also were remained constant during the run.[2] Since the contact time is quite short in the present system, the isomerization between three isomers is not supposed to take place, as is observed over the Lewis catalysts such as $AlCl_3$ or BF_3. In the case of BF_3, the products are 45.1% *o*-, 21.5% *m*-, and 33.0% *p*-isomers (*6*). Thus, the formation of para isomer predominates over the present catalysts.

Iron sulfate is decomposed to form iron oxide above 500°C. In fact, it was shown that both ferrous and ferric sulfates are still mainly kept in sulfate forms at 500°C of calcination, but decompose to form iron oxides containing 0.15% of sulfur at 700°C (*5*). No sulfur was contained when calcined at 900°C. By means of X-ray diffraction and Mössbauer spectrum, ferrous sulfate was observed to consist of α-Fe_2O_3 and $Fe_2(SO_4)_3$ in the ratio of 1 and 2, respectively, at 500°C and change to form completely α-Fe_2O_3 above 700°C (*5*). However, the benzylation reaction over Fe_2O_3 heat-treated at 700°C was 40 times as slow as that of $Fe_2(SO_4)_3$ calcined at the same temperature (*3*). In order to have more information concerning the effects of calcining temperature on catalyst behavior, studies by X-ray photoelectron spectroscopy are being performed.

In order to obtain information about the reaction mechanism over the present catalyst, as usually studied for the Friedel-Crafts reaction, the relative rate of toluene to benzene, k_T/k_B, and partial rate factors, o_f, m_f, p_f, were determined. The latter factors indicate the positional relative rate of reaction of benzene and toluene, calculated from k_T/k_B and isomer ratio.

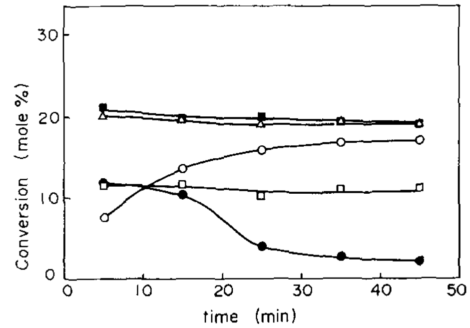

FIG. 1. Isopropylation of toluene with isopropy bromide over calcined iron sulfate at 150°C. $Fe_2(SO_4)_3$ (600°C) (●); $Fe_2(SO_4)_3$ (800°C) (○); $Fe_2(SO_4)_3$ (700°C) (△); $FeSO_4$ (700°C) (■); $FeSO_4$ (700°C) with isopropyl chloride (□): the calcination temperature of catalyst is given in parentheses.

The k_T/k_B from competitive reaction using isopropyl bromide as alkylating agent and $FeSO_4$ (calcined at 700°C) as catalyst was observed to be 2.21 at 150°C.[3] The value was independent of reaction time; i.e., 2.40, 2.10, 2.10, 2.15 and 2.21 for the reaction periods of 0–10, 10–20, 20–30, 30–40 and 40–50 min, respectively. Using 2.21 of k_T/k_B, partial rate factors were calculated to be $o_f = 2.39$, $m_f = 1.54$ and $p_f = 5.37$.

The k_T/k_B value is in relatively good agreements with Olah and co-workers' 1.68 (*7*) or 1.65 (*8*) obtained using $GaCl_3$ or $AlCl_3$ as catalyst and Brown and Smoot's 1.82 (*9*) with $GaBr_3$, but not in harmony with the recent reported one by Nakane *et al.* (*6*). From competitive and noncompetitive studies using isopropyl fluoride and BF_3, they obtained $k_T/k_B \sim 0.7$ in two nonpolar solvents; cyclohexane and *n*-hexane. Recently, Carter and co-worker's (*10*) careful studies of kinetics showed $k_T/k_B = 3.7$ for an ethylation of toluene with ethyl bromide in nonpolar solvent with $AlBr_3$ as catalyst. Rather scattered values may be due to the side reactions, as

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[2] The reaction with isopropyl chloride over $Fe_2(SO_4)_3$ (700°C) at 150°C gave 36.0, 20.0 and 44.0 with 0–10 min and 36.1, 22.7 and 41.2% with 40–50 min for *o*-, *m*-, and *p*-isomer, respectively.

[3] At 115°C of the reaction temperature under the same conditions, k_T/k_B was 2.40, and isomers were *o*- = 35.3, *m*- = 22.6 and *p*- = 43.1%.

pointed out by Carter *et al.* (*10*). However, in the present reaction system, the side reactions such as disproportionation and isomerization could not occur. Thus, our k_T/k_B values seem to be more reasonable.

The present type of catalyst shows high selectivity with quite low possibility of side reactions and has advantages of separating products from a catalytic amount of the catalyst with much ease. These facts have never been reported in the field of the Friedel-Crafts reaction.

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