REACTION OF CARBON DIOXIDE WITH TOLUENE IN THE PRESENCE OF ALUMINUM CHLORIDE UNDER PRESSURE

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UDC 542.97:541.12.034:546.262.3-31:
547.533

Many investigations have been devoted to the reactions for the carboxylation of aromatic hydroxy and amino compounds with carbon dioxide [1]. Very little data exists on the carboxylation of benzene and its nearest homologs. Thus, in [2] it was established that small amounts of benzoic acid are formed from benzene and CO_2 in the presence of $AlCl_3$; the formation of toluic acid from toluene and CO_2 in the presence of zinc–copper–chromium catalyst is mentioned in [3]; in [4] it is indicated that benzoic acid is obtained in low yield (6%) from benzene and CO_2 at a pressure of 40 atm in the presence of $AlCl_3$, along with the simultaneous formation of ketones in a yield of up to 3.5%. In the absence of a catalyst the reaction of benzene with CO_2 failed to go even at ultrahigh pressures. In [5] only toluic acid was isolated from the reaction products of CO_2 with toluene in the presence of $AlBr_3$.

Since many reactions, catalyzed by aluminum halides, are activated by a hydrogen halide, a study was made of the effect of HBr on the carboxylation of triethylbenzene with CO_2 [6]. It was established that the reaction failed to go when the complex $Al_2Br_6 \cdot C_6H_3(C_2H_5)_3 \cdot HBr$ was allowed to stand with CO_2 for 50 h at 50°C. The complex $Al_2B_2[C_6H_3(C_2H_5)_2]$ gave a very low yield of the carboxylic acid and the ketone, while only traces of the ketone were obtained from the complex $Al_2Br_6 \cdot 3[C_6H_3(CH_3)_3] \cdot HBr$, and the acid was not isolated. Apparently, the complex $AlBr_3 \cdot$ hydrocarbon $\cdot\, CO_2$ was formed during the reaction process, in which connection the presence of the hydrogen halide prevented the carboxylation reaction. $AlCl_3$ gave complexes with aromatic hydrocarbons more easily than did $AlBr_3$ [5].

In the present paper we studied the reaction of CO_2 with toluene in the presence of $AlCl_3$ at 50-125° and a CO_2 pressure of 20-50 atm under static conditions. The obtained results are summarized in Table 1. The principal reaction products were p-toluic acid, ditolyl ketones, benzene, and high-molecular compounds, which were not investigated more closely. The yields of p-toluic acid, formed according to the reaction: $C_6H_5CH_3 \xrightarrow{CO_2} p\text{-}CH_3C_6H_4COOH$, reached 23%. The ditolyl ketones, the formation of which goes according to the reaction: $2C_6H_5CH_3 \xrightarrow{CO_2} CH_3C_6H_4COC_3H_4CH_3 + H_2O$, were obtained in up to 30% yield. The benzene was formed as a result of the disproportionation: $2C_6H_5CH_3 \rightarrow C_6H_6 + C_6H_4(CH_3)_2$.

A similar reaction was also observed earlier at atmospheric pressure in the absence of CO_2 [7]. The yields of benzene in our experiments reached 16%. Traces of xylenes were detected in the reaction products. Since the reaction rate with CO_2 decreases in the order [6]: xylenes > toluene > benzene, the xylene was converted to high-molecular products, the yield of which reached 12.5%, while the formed benzene practically failed to react with CO_2.

The reaction course and the composition of the products are both markedly affected by the reaction temperature, CO_2 pressure, reaction time, and the amount of taken $AlCl_3$ catalyst (see Table 1). A study of the effect of the amount of catalysts (Expts. 1-4) disclosed that the yields of p-toluic acid and benzene are maximum when 15 g of $AlCl_3$ is used, while the yields of the ditolyl ketones and high-molecular compounds are maximum when 37 g of $AlCl_3$ is used. In the subsequent experiments we used 15 g of $AlCl_3$.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.4, pp. 967-969, April, 1972. Original article submitted May 20, 1971.

TABLE 1. Reaction of Carbon Dioxide with Toluene in the Presence of $AlCl_3$

Expt. No.	Amount of catalyst, g	Reaction time, h	Reaction temperature, °C	CO_2 pressure, atm	Yield, in % when based on starting toluene			
					p-toluic acid	ditolyl ketones	benzene	high-molecular compounds
1	4	6	100	50	3,1	11,5	3,6	0,9
2	15	6	100	50	15,2	14,0	16,4	5,2
3	26	6	100	50	10,1	24,7	14,6	7,2
4	37	6	100	50	6,4	25,4	14,6	12,4
5	15	1	100	50	22,6	11,0	10,1	3,6
6	15	3	100	50	18,1	17,5	13,1	2,8
7	15	6	100	50	15,2	14,0	16,4	5,2
8	15	12	100	50	15,3	20,0	9,9	12,4
9	15	1	50	50	0	0	0	0
10*	15	1	75	50	8,0	10,0	2,6	0,7
11	15	1	125	50	3,6	34,5	11,0	3,3
12	15	1	100	20	7,3	18,1	5,4	2,7
13*	15	1	100	35	8,7	20,5	9,2	3,1

*Also see Expt. 5.

When the reaction time is increased from 1 to 12 h (Expts. 5-8) the yield of p-toluic acid drops from 22.6% (maximum yield in our experiments) to 15.3%, while the yield of the ditolyl ketones, in contrast, increased by 9%, and the yield of the high-molecular compounds increased by the same amount, whereas the yield of benzene was maximum at a reaction time of 6 h.

The effect of the reaction temperature was studied in the range 50-125°, and the effect of pressure was studied in the range 20-50 atm, with a reaction time of 1 h (Expts. 5 and 9-11, and correspondingly 5 and 12-13). The maximum yield of p-toluic acid was obtained at 100° and 50 atm of CO_2, while the maximum yield of the ditolyl ketones was obtained at 125° and 50 atm. Benzene was also formed in the highest yield under these conditions. A decrease in the temperature below 100° sharply lowers the yield of high-molecular compounds, while at 100-125° the yield is practically independent of the CO_2 pressure in the investigated range.

The obtained data show that in the presence of at least 15 g of catalyst, a temperature of at least 100°, and a pressure of at least 50 atm, the sum of the yields of p-toluic acid and ditolyl ketones is a nearly constant value, and is 30-35% when based on the starting toluene. An antibatic change in the yields of these compounds is observed with increase in the reaction time: a decrease in the yield of p-toluic acid and an increase in the yield of ditolyl ketones. These results make it possible to assume that the ditolyl ketone is probably formed from the toluic acid, and consequently this explains the predominant amount of p-ditolyl ketone in the ketones fraction. The disproportionation of toluene with the formation of benzene goes to a slight degree at temperatures below 100° and pressures below 35 atm. A small amount of high-molecular compounds is formed under these conditions, which is apparently explained by their formation from the xylenes that are obtained simultaneously with the benzene by the disproportionation of toluene.

EXPERIMENTAL

The experiments were run in a rotated 0.25-liter autoclave. For reaction we took 0.28 mole of toluene. At the end of experiment the reaction products were dumped on cracked ice and extracted with ether. The ether extract was treated with 200 ml of 10% KOH solution, washed with water until neutral, and dried over $CaCl_2$. The alkaline solution was combined with the wash waters and acidified with 10% HCl solution to pH 2-3. The liberated p-toluic acid was filtered, dried in the air, and then sublimed, mp 176.5-177.5°; from [8]: mp 176-178°. Found: C 70.55; H 6.21%. $C_8H_9O_2$. Calculated: C 70.59; H 5.88%. The UV spectrum of the toluic acid corroborated the p-substitution: λ_{max} 238 nm, ε 14274, log ε 4.15544, λ_s 276 nm, ε 793, λ_s 285 nm, ε 550. From [9]: p-toluic acid has λ_{max} 236 nm and log ε 4.14.

The ether extract was subjected to fractional distillation. A fraction with bp 140-160° (2 mm) was isolated. Found: C 85.91; H 7.03%. $C_{15}H_{14}O$. Calculated: C 85.71; H 6.67%. The UV spectra of the fraction coincide with the spectrum of the ditolyl ketones given in [10].

CONCLUSIONS

1. When toluene is reacted with CO_2 in the presence of $AlCl_3$ at a pressure of 20-50 atm and temperatures of 77-125° the toluene is carboxylated to p-toluic acid in up to 23% yield. At the same time are formed ditolyl ketones in up to 35% yield and benzene in up to 16% yield.

2. Disproportionation of the toluene to benzene and xylenes occurs during the indicated reaction, and also the formation of ditolyl ketones via toluic acid.

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