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ALKYLATION BEHAVIOR OF WCl_6, $MoCl_5$ AND THE METHATHESIS COCATALYST SYSTEM WCl_6-$C_2H_5AlCl_2$

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Recently, Calderon and co-workers reported (1) the intriguing discovery that WCl_6 treated with $C_2H_5AlCl_2$ in benzene catalyzes olefin methathesis. For example, 2-pentene is converted to a mixture of 25% 2-butene, 50% 2-pentene, and 25% 3-hexene. Kothari and Tazuma (2) observed an unexpected behavior of the WCl_6-$C_2H_5AlCl_2$ catalyst when it was preformed in toluene: upon addition of 2-pentene, Friedel-Crafts alkylation of toluene resulted instead of the anticipated methathesis reaction which occurs when the catalyst is prepared in toluene in the presence of an olefin. Benzene alkylation proceeded more slowly and was accompanied by an even slower 2-pentene methathesis. We wish to report data that illuminate the alkylation properties of WCl_6, $MoCl_5$ and WCl_6-$C_2H_5AlCl_2$ and show that WCl_6 can promote alkylation under certain conditions in the absence of $C_2H_5AlCl_2$.

Tungsten hexachloride in the absence of $C_2H_5AlCl_2$ readily promotes the alkylation of benzene with propylene at 150°.* With 40% of the benzene converted the alkylated product consisted of 55% cumene, 31% diisopropylbenzene (mixture of isomers), and 14% triisopropylbenzene. Slow alkylation occurs at 100°. Similarly, alkylation of benzene occurs with 1-pentene. The catalyst exhibits selectivity for substituted olefins. With an equimolar mixture of ethylene and 1-butene and with 31% of the benzene converted, the alkylation product consisted of 13% ethylbenzene, 58% *sec*-butylbenzene, and 29% di-*sec*-butylbenzene.

The reaction takes a different course with ethylene as shown by the data in Table I.

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*Catalyst concentration usually was 1.3×10^{-3} molar. WCl_6 was purified as described elsewhere (1). All reagents were carefully dried. The olefin was always added to the autoclave last.

Table I. WCl_6-PROMOTED ALKYLATION OF BENZENE WITH ETHYLENE[a)]

Reaction Time, hr.	0.25	1.0	2.0	5.0
Benzene Conversion, % mole	3.2	6	20	34
Yields, %				
Ethylbenzene	0	0	5	14.6
<u>sec</u>-Butylbenzene	2.8	4.5	9	12.6
di-<u>sec</u>-Butylbenzene	0.4	1.5	6	6.8

a) Conditions: benzene, 27 g, WCl_6 concentration, 1.26×10^{-3} moles/l.; temperature, 160°C, ethylene pressure, 600 psi.

Tungsten hexachloride promotes the dimerization of ethylene to butenes which subsequently alkylate benzene. In an inert solvent (diethyl ether) with benzene absent, ethylene was shown to dimerize as the catalyst solution was heated to the temperature employed for alkylation. The butenes, being more reactive, compete more favorably than does ethylene for benzene; consequently, mainly <u>sec</u>-butylbenzenes are produced during the early stages of the alkylation reaction.* As the reaction proceeds, the dimerization activity appears to abate and alkylation with ethylene becomes more predominant. In some instances, small amounts of polymer also were concomitantly formed from ethylene.

Ethylaluminum dichloride enhances the rate of alkylation. With only one mole of $C_2H_5AlCl_2$ present for 2.5 moles of WCl_6, the rate of alkylation of benzene with ethylene at 60° was roughly the same as that observed at 150° when $C_2H_5AlCl_2$ was not present. Perhaps, the very active alkylation catalyst $AlCl_3$ was produced <u>in situ</u> from the reaction of $C_2H_5AlCl_2$ with WCl_6.

Molybdenum pentachloride is a more active alkylation catalyst than WCl_6. Like the latter, it produces mainly <u>sec</u>-butylbenzene at low benzene conversions but tends to form more polymeric by-product from the ethylene co-reactant.

Tungsten hexachloride also is a transalkylation catalyst. When WCl_6 was contacted with ethylbenzene at 160° for 17 hr., a mixture of benzene, ethylbenzene and diethylbenzenes was produced. WCl_6 is ineffective for the transalkylation reaction between benzene and xylenes.

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*<u>sec</u>-Butylbenzene from benzene and ethylene also results in the presence of rhenium pentachloride (3).