

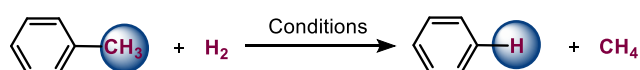
Selective Hydrodemethylation of Methyl Alkylbenzenes with Carbon-Supported Potassium Hydride

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Benzene, toluene, xylenes (BTX) and higher alkylated aromatics are essential petrochemicals, and their production is balanced according to the demand using the hydrodemethylation (HDM) and, more generally, the hydrodealkylation (HDA) process, as well as the isomerization of xylenes and transalkylation processes. We have recently reported that the HDM of toluene to benzene proceeds when a catalytic amount of carbon-supported potassium hydride (KH/C) is heated in neat toluene to ca. 250 °C under 50–80 bar H₂ (for the industrial HDM process, a higher temperature of ca. 480–590 °C is used in combination with a transition metal catalyst, Scheme 1A).^[1] In contrast, the transalkylation reaction relies on an acid catalyst and follows the Friedel-Crafts mechanism. The propensity to transalkylation of tertiary, secondary and primary alkyl groups is governed by the stability of the respective carbocations, i.e., 3° > 2° > 1° > CH₃.^[2] Here, we studied HDA of various methyl alkylbenzenes with [KH/C + H₂] and found a selective HDM in preference to HDA for the removal of CH₃, C₂H₅, *i*-C₃H₇, *t*-C₄H₉, and *c*-C₆H₁₁ substituents (Scheme 1B). That is, a [KH/C + H₂] reactive system provides the opposite reactivity trend to that observed in the Friedel-Crafts transalkylation, i.e., CH₃ > 1° > 2° > 3° alkyl substituent, suggesting a different mechanism, possibly involving radical species. We tentatively ascribe this HDM activity to result from the dissociation of H₂ on the potassium radical anion salts of the respective aromatic substrates. The formed hydrogen radical species then may serve as a chain transfer reagent (Scheme 1C).

A. Previous work



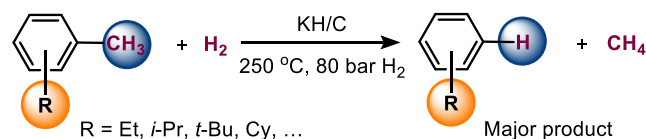
Industrial HDM of toluene:

480–590 °C, 40–60 bar H₂, CrO_x/MoO_x or supported Pt

Our approach:

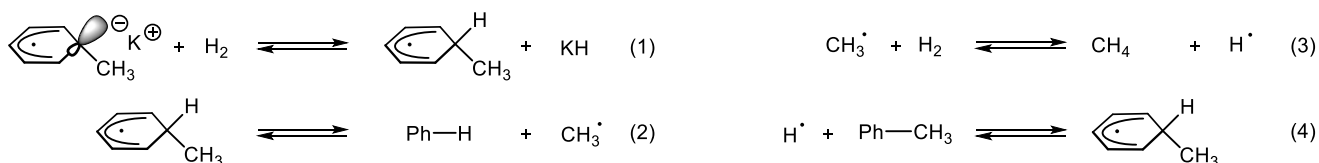
ca. 250 °C, 50–80 bar H₂, catalytic amount of KH/C

B. This work



Selective hydrodemethylation of methyl alkylbenzenes

C. Possible elementary steps (1-4)



Scheme 1. Industrial and emerging approaches to the HDM of toluene (A), selective HDM of methyl alkylbenzenes studied in this work (B), and conceivable steps involved in the developed HDM methodology with KH/C.

[1] F. Chang, A. Fedorov, *ChemSusChem* **2023**, *16*, e202202029.

[2] R. M. Roberts, E. K. Baylis, G. J. Fonken, *J. Am. Chem. Soc.* **1963**, *85*, 3454–3458.