

Production of Benzene by the Hydrodemethylation of Toluene with Carbon-Supported Potassium Hydride

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The hydrodemethylation (HDM) of toluene to benzene is an industrial process performed at elevated temperatures ($\approx 500^\circ\text{C}$ and higher). Here, it was reported that heating graphite-supported potassium hydride (KH/C) with toluene under H_2 atmosphere provided benzene already at $125\text{--}250^\circ\text{C}$. Depending on the H_2 pressure, the reaction was either substoichiometric (≤ 11 bar) or catalytic (≥ 50 bar) with respect

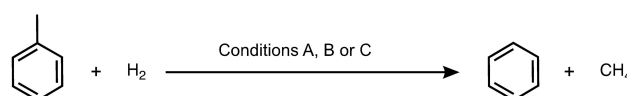
to KH, indicating that KH may serve as a radical chain initiator. At 250°C , the selectivity to benzene was 98 and 63% when using 6 and 80 bar of H_2 , respectively, owing to the competing formation of cyclohexane and methylcyclohexane at high H_2 pressure. The used KH/C material was amenable to recycling without a notable loss in the yield of benzene.

Introduction

Benzene is an essential chemical for the synthesis of a host of value-added products that range from medical drugs to lubricants, polymers, detergents, and so on.^[1] A large volume of benzene is made by the hydrodemethylation (HDM) of toluene and xylenes. According to a report by the U.S. Department of Energy, more than a half of produced toluene is subsequently used in the manufacture of benzene by an HDM process.^[1] In particular, the Houdry Detol process produces benzene by combining streams of toluene and hydrogen, typically at $480\text{--}590^\circ\text{C}$ and at pressures of 40–60 bar, over a heterogeneous catalyst comprising oxides of Cr or Mo, or supported Pt (Pt/SiO₂, Pt/Al₂O₃, Scheme 1).^[1,2] Since the HDM of toluene is exothermic, it can proceed also at lower temperatures, however, at the expense of catalyst deactivation.^[1,2]

A viable alternative to the Houdry Detol process is the thermal (uncatalyzed) hydrodemethylation of toluene. Yet it requires an even higher temperature ($\approx 700\text{--}900^\circ\text{C}$).^[3,4] necessary to dissociate H_2 to hydrogen radicals and form thereby the chain transfer species of this reaction.^[5,6] Overall, owing to the high operating temperatures, both catalyzed and uncatalyzed HDM are energy-intensive and, thus, costly processes. That being said, a more sustainable methodology that relies on a low-temperature HDM of toluene is currently lacking.

The injection of an electron into the antibonding orbitals of aromatic hydrocarbons notably eases the cleavage of certain



Industrial HDM of toluene

- A. $480\text{--}590^\circ\text{C}$, 40–60 bar, catalyst: CrO_x, MoO_x or supported Pt (Pt/SiO₂, Pt/Al₂O₃)
B. $700\text{--}900^\circ\text{C}$, atmospheric pressure, H \cdot as chain transfer species

This work

- C. $125\text{--}250^\circ\text{C}$, 1–80 bar H_2 , substoichiometric KH/C

Scheme 1. Approaches to the hydrodemethylation of toluene.

C–C bonds; namely, dianions formed from 1,2-diarylethanes (ArCH₂CH₂Ar) and Cs–K–Na alloy are susceptible to the cleavage of the central C(sp³)–C(sp³) bond that yields benzyl anion salts at -75°C .^[7] Several related reactions have been reported.^[8–13] The demotion of electrons from the antibonding orbitals in the alkali metal adducts (typically, dianions) to the bonding orbitals of the products drives those reactions, aided by the relative thermodynamic stability of the formed benzyl anion salts. However, such requirements constrain the substrate scope mostly to di- and polyarylated derivatives of methane and ethane and exclude simple aromatics such as toluene. In addition, discussed “dissolving metal” reductions necessitate the complexation of an alkali ion by a crown ether,^[14–16] or a coordinating solvent (diglyme, tetrahydrofuran).^[17] We report herein that under 80 bar of H_2 and in the absence of any coordinating additives, neat toluene (1) yields benzene (2) when heated to 250°C with potassium supported on graphite (K/C). Competing products are cyclohexane (3) and methylcyclohexane (4). The yield of 2 increases by around twenty times if graphite-supported potassium hydride (KH/C) is used in place of K/C. In the latter conditions, the molar amount of formed 2 exceeds the molar amount of used KH by more than twelve times, in agreement with a radical chain reaction initiated by catalytic amounts of KH.

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Results and Discussion

Initially, we assessed the HDM activity of several alkali-based reagents using neat **1** at 250 °C (20 h) in a batch reactor filled at room temperature to 80 bar H₂ (at 250 °C, the total pressure increases to 128 bar). Toluene was degassed by three freeze–pump–thaw cycles and used without drying. The gas chromatography mass spectrometry (GC–MS) analysis of the reaction mixtures (no work up) detects **4** as the only product when KOtBu,^[18] a 1:1 mixture of KOtBu and Et₃SiH,^[19,20] potassium bis(trimethylsilyl)amide (KHMDs), or a commercial silica-supported sodium-potassium alloy K₂Na/SiO₂ are used.^[21] However, the molar amounts of **4** correspond to merely 1–10% of the used potassium reagents (Table 1, entries 1–4).^[22] Utilizing metallic potassium or K/C (≈ 30 wt% loading of K on C) under an argon atmosphere gives no detectable products (Table 1, entries 5 and 6). However, if the Ar atmosphere is replaced by H₂, the HDM products **2** and **3** form along with **4**. In particular, K/C under 80 bar H₂ gives the partial selectivity to benzene (i.e., the selectivity among the quantified products **2–4**) of 69% and the amount of formed **2** corresponds to 0.59 molar equiv. of potassium in the utilized K/C (Table 1, entry 7).

Since K/C transforms to KH/C under an H₂ atmosphere,^[23] we tested commercial KH and graphite-supported KH (obtained from 30 wt% K/C and H₂) in the HDM of toluene.^[24] Both materials gave products **2–4** but with notably different yields; the amount of benzene obtained using KH/C was around sixty times higher than that with commercial KH (Table 1, entries 8 and 9). Interestingly, 12.2 equiv. of **2** form per 1 equiv. of potassium hydride in KH/C, suggesting that the HDM of toluene may be initiated by KH and proceed in those conditions by a radical chain mechanism. In contrast, under an argon atmosphere KH/C yields only minor amounts of **2** and **4** (Table 1, entry 10). To summarize, our initial screening of the alkali

Table 1. Initial screening of alkali reagents for the HDM of toluene (250 °C, 20 h).

Entry	Reagent ^[a]	Gas phase	$\chi^{[b]}$ [%]	$S^{[c]}$ 2 [%]	$R^{[d]}$ 2	Mol 2/3/4 to mol K
1	KOtBu	H ₂	0.01	0	0	0:0:0.01
2	KOSi ^[e]	H ₂	0.01	0	0	0:0:0.01
3	KHMDs	H ₂	0.04	0	0	0:0:0.05
4	K ₂ Na/SiO ₂	H ₂	0.1	0	0	0:0:0.1
5	K	Ar	0	0	0	0:0:0
6	K/C	Ar	0	0	0	0:0:0
7	K/C	H ₂	0.7	69	0.03	0.59:0.07:0.19
8	KH ^[f]	H ₂	0.3	50	0.01	0.19:0.02:0.17
9	KH/C	H ₂	15.3	63	0.61	12.2:2.19:4.93
10	KH/C	Ar	0.02	66	0.001	0.02:0:0.01

[a] In entries 1–3 and 5–10, the used alkali reagent contained 15 mg of potassium. In entry 4, K₂Na/SiO₂ contained 15 mg of potassium and sodium (2:1 molar ratio). Volume of toluene was 5 mL. Pressures of H₂ and Ar at room temperature were 80 and 11 bar, respectively. [b] Conversion is calculated based on yields of **2–4**. [c] Selectivity among **2–4**. [d] Apparent production rate, expressed as mol (**2**) × mol (KH)⁻¹ × h⁻¹. [e] KOSi stands for a 1:1 mixture of KOtBu and Et₃SiH. [f] Commercial KH.

reagents and the gas atmosphere identified a combination of KH/C and H₂ as promising towards the low-temperature HDM of toluene.

Next, we evaluated how the reaction temperature, H₂ pressure, reaction time, and the weight loading of KH on the graphite support influence the yield and selectivity to benzene. We refer to the Supporting Information for additional details and experiments (Figures S4–S9, Table S1). In brief, under 80 bar H₂, the HDM of toluene proceeds already at 125 °C, although at this temperature the formation of benzene is substoichiometric with respect to the amount of potassium hydride in the used KH/C (Table 2, entry 1). The yield of **2** at 250 °C is around forty times higher than at 125 °C while the partial selectivity to **2** is only moderately lower (71 and 63%, respectively; Table 1, entry 9, Table 2, entry 1, and Figure 1A). Selectivity to benzene is 98% at 6 bar H₂ (Table 2, entry 2) and declines with the H₂ pressure owing to the competing hydrogenation to **3** and **4** (Figure 1B). Selectivity to **2** is also higher at shorter reaction times (Figure 1C), that is, 85% after only 3 h at

Table 2. Selected optimization results for the HDM of neat toluene (5 mL) with 50 mg of 30 wt% KH/C (0.8 mol% KH loading with respect to toluene).

Entry	$P(\text{H}_2)$ [bar]	T [°C]	t [h]	$\chi^{[a]}$ [%]	$S^{[b]}$ 2 [%]	$R^{[c]}$ 2	Mol 2/3/4 to mol KH
1	80	125	20	0.3	71	0.02	0.30:0.01:0.11
2	6	250	20	0.6	98	0.04	0.79:0:0.02
3	80	250	3	3.0	85	1.06	3.20:0.14:0.45
4	50	250	20	7.7	70	0.30	5.93:0.37:2.23

[a] Conversion is calculated based on yields of **2–4**. [b] Selectivity among **2–4**. [c] Apparent production rate, expressed as mol (**2**) × mol (KH)⁻¹ × h⁻¹.

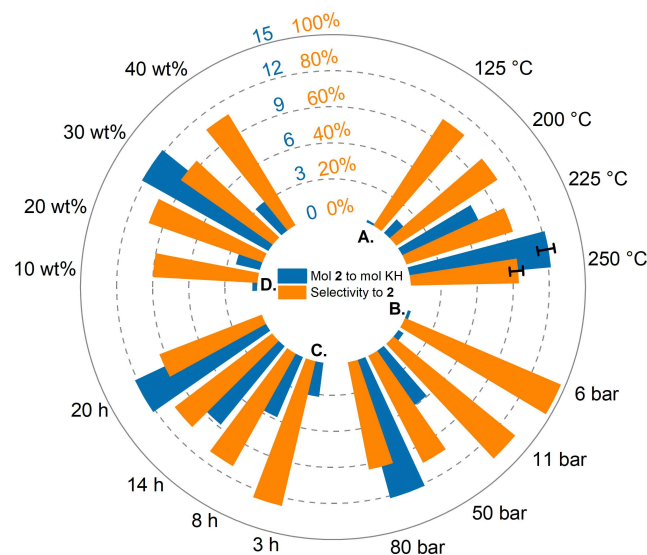


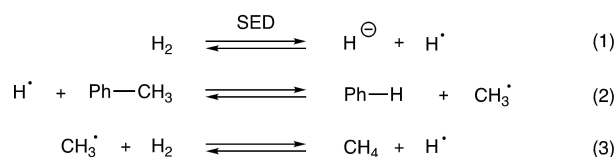
Figure 1. Selectivity to benzene and the amount of formed benzene relative to the amount of used potassium hydride in KH/C in the HDM of toluene under H₂ atmosphere (orange and blue bars, respectively). Parameters varied were (A) reaction temperature, (B) H₂ pressure, (C) reaction time, and (D) the weight loading of KH in KH/C. One parameter was modified at a time relative to the standard conditions (250 °C, 80 bar H₂, 20 h, 30 wt% KH/C). See Table S1 for details.

250 °C under 80 bar H₂ (Table 2, entry 3). The yield of **2** increases with the H₂ pressure such that the amount of formed **2** exceeds the amount KH in KH/C by 5.9 and 12.2 times at 50 and 80 bar, respectively (Table 2, entry 4 and Table 1, entry 9). In the latter experiment, products **2–4** account for 15.3% toluene conversion and 9.7% yield of **2**, achieved using only 0.8 mol% KH/C.

Interestingly, the amount of formed **2** relative to the amount of used KH shows a volcano-type dependence when the weight loading of KH on C is varied from 10 to 40 wt%, reaching maximum at around 30 wt% loading (50 mg of KH/C was used with 5 mL of toluene, Figure 1D, Table S1). The increasing yield of benzene with the KH loading on C, at least in part, may be related to the reaction between KH and traces of water in toluene (which is used degassed but not dried). However, the decreasing yield of benzene with the KH loading could be related to the crystallite size of KH, which is larger in 40 wt% KH/C relative to 30 wt% KH/C (≈46 vs. 39 nm estimated according to the Scherrer equation, Figure S10). Indeed, reactions with KH are known to be exclusively surface reactions, and the surface area is expected to decrease with the increasing crystallite size.^[25]

Experiments performed with the recovered KH/C in the standard conditions (see caption to Figure 1) show that the amount of formed **2** relative to the amount of initial KH decreases, from the first to the third cycle, by around 14%, but the selectivity to **2** increases by 23% (Figure S11). These changes can be due to the modification of the potassium phase by carbonaceous species. Consistent with this rationale, when the HDM of **1** is performed in octane solution, the reaction carbon balance, at 81% toluene conversion and using a 1:1 molar ratio of 1/KH, is only around 80%, indicating adsorption of **1** (or its products) onto KH/C (Scheme S1). No demethylation of **4** was observed in octane solution using the standard conditions (Scheme S2).

The elementary steps and the nature of reactive intermediates in the HDM reaction developed here are currently understudied. We tentatively hypothesize that a radical chain mechanism can be involved with the hydrogen radical species (H•) responsible for the chain transfer steps (Scheme 2).^[26] This hypothesis is supported by the previous mechanistic studies of a reaction between sodium naphthalenide and H₂, which yields naphthalene and an “exceedingly active” form of NaH.^[27] The mechanism for the latter reaction is suggested to include a single electron transfer (SET) from Na⁺C₁₀H₈^{•-} to H₂ that generates NaH, H•, and naphthalene.^[28] In our case, a strong electron donor to enable SET to H₂ (such as the potassium biphenyl dianion salt) can form by the interaction of KH with



Scheme 2. Possible steps for the HDM of toluene using KH/C and H₂. The nature of a conceivable strong electron donor (SED) for Equation (1) has been discussed in Ref. [29].

benzene (or toluene) via mechanisms discussed by Murphy and co-workers.^[29]

It could be argued that potassium radical anion species, K⁺C₇H₈^{•-}, may also play a role in the HDM mechanism. However, we note that no methyl group cleavage has been reported, in the absence of H₂, for the potassium adduct of toluene with dicyclohexano-18-crown-6, although this reagent has been explored for the removal of functional groups (fluorides, nitriles, etc.),^[30–32] and the thermal transformations of a related potassium toluene adduct have been studied.^[14] Lastly, biphenyl (a common product of the industrial HDM of toluene) and 1,2-diphenylethane were not detected in any of experiments in this work, suggesting that the intermediate formation of phenyl and benzyl radicals is not likely. Since xylenes and ethylbenzene (expected products of methyl radical reactions) were not observed either, the HDM of toluene likely proceeds via an inner sphere (with respect to toluene) mechanism.

Work is currently underway to extend this chemistry from batch to gas-phase flow experiments, as well as to understand the scope of the alkyl groups amenable to the developed hydrodealkylation methodology using KH/C with H₂.

Conclusion

We have reported a novel methodology for the hydrodemethylation (HDM) of toluene to benzene that is enabled by KH supported on graphite. KH/C is required in only catalytic quantities when H₂ pressure in excess of around 50 bar is used, and KH/C can be recycled without a notable loss in the yield of benzene. While our approach is complementary to the established industrial HDM methods, it compares to those methods favorably due to the use of notably lower reaction temperatures (125–250 °C).

Experimental Section

In an N₂-filled glovebox, 15–87 mg of potassium-containing materials (KH/C, K/C, K, KOtBu, KOSi reagent comprising KOtBu and Et₃SiH in a 1:1 molar ratio, KHMDS, commercial KH or K₂Na/SiO₂) and 5 mL of toluene were added into an autoclave equipped with a glass liner. The autoclave was sealed, brought out from the glovebox, and connected to a high-pressure line of Ar or H₂. The line was purged (3 times with 11 bar of Ar or 100 bar H₂) and the autoclave pressurized to a set pressure of Ar or H₂ and heated to the desired temperature (ramping rate was 5 °C min⁻¹). Unless specified otherwise, the stirring rate was 500 rpm. Except for the recycling experiments, after the test the reaction mixture was open in air, filtered (filter paper), and the supernatant collected and analyzed by GC-MS (after adding a known amount of tridecane internal standard). For the recycling experiments, after a test the autoclave was transferred into the N₂-filled glovebox. The liquid part of the reaction mixture was collected for the GC-MS analysis, and a new batch of toluene (5 mL) was added for the subsequent test.

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Conflict of Interest

A patent application based on the results described in this work has been filed.

Data Availability Statement

The data that support the findings of this study is available in the supplementary material of this article and from the corresponding author upon reasonable request.

Keywords: hydrodemethylation · potassium hydride · radical anions · single electron transfer · toluene

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