

The Formation of Gas Phase Benzyl Radicals during the Reaction of Toluene and Nitrous Oxide over Li-MgO and Sr-La₂O₃ Coupling Catalysts

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Surface-generated gas-phase benzyl radicals have been detected during the reaction of toluene and nitrous oxide over Li-MgO and Sr-La₂O₃ catalysts.

There is extensive evidence that the oxidative coupling of methane to form ethane, and subsequently ethylene, involves surface-generated gas-phase methyl radicals.¹ The equally interesting cross coupling of methane with toluene to form ethylbenzene, and subsequently styrene, presumably occurs via an analogous mechanism; however, there are no reports of benzyl radicals being formed over effective catalysts.³⁻⁶ In fact, Suzuki *et al.*⁴ suggest that the coupling occurs on the surface, rather than in the gas phase. Since the methyl C-H bonds are weaker in toluene (364 kJ mol⁻¹) than in methane (431 kJ mol⁻¹), one might expect that benzyl radicals would be formed more readily than methyl radicals. Nevertheless, it is conceivable that the benzyl radicals would be held more strongly to the surface through their π electrons.

We report here the first spectroscopic evidence for the formation of benzyl radicals over a catalyst that is active and selective for the cross-coupling reaction. The radicals were produced during the catalytic reaction of C₆H₅CH₃ and N₂O over Li-MgO and Sr-La₂O₃ catalysts at 650 °C. A matrix isolation electron spin resonance (MIESR) system was used to collect and detect the radicals.⁷ Briefly, the reagent gases plus Ar, at a pressure of about 1 Torr, flow over the hot catalyst and then through a leak into a differentially pumped region. The radicals are trapped in an Ar matrix on a cold sapphire rod and are detected by ESR spectroscopy. In the present study three catalysts were used: one was composed of 4 mass% Li⁺ on

MgO, another of 1 mass% Sr²⁺ on La₂O₃, and the third was pure Sm₂O₃. The Li-MgO catalyst was prepared from an aqueous slurry of Li₂CO₃ and MgO; the Sr-La₂O₃ catalyst was obtained from Amoco. The catalysts were pretreated in flowing O₂ for 40 min at 700 °C before they were cooled to 650 °C. A gas mixture of Ar/C₆H₅CH₃/N₂O = 4.8/0.1/0.1 cm³ min⁻¹ was passed over the catalysts.

The ESR spectrum of benzyl radicals, formed over the Li-MgO catalyst, is shown in Fig. 1(a). The experimental spectrum is in good agreement with a simulated spectrum [Fig. 1(b)], which was obtained using published parameters: $g = 2.0027$, $a(\text{CH}_2) = 16.34$ G, $a_o^H = 5.13$ G, $a_m^H = 1.77$ G, $a_p^H = 6.17$ G.⁸ Here, $a(\text{CH}_2)$, a_o^H , a_m^H and a_p^H are the hyperfine splitting constants for the CH₂, *ortho*-, *meta*- and *para*-protons. The small peak at $g \approx 2.03$ is assigned to peroxy radicals that result from the reaction of hydrocarbon radicals with O₂. The latter was produced by the decomposition of a small amount of N₂O. The good agreement between spectra a and b confirms that benzyl radicals were indeed formed over the Li-MgO catalyst at a temperature typically used in oxidative coupling, and that they emanated into the gas phase. When O₂ was used in place of N₂O, but at a flow rate of 0.025 cm³ min⁻¹, the broad ESR spectrum of benzyl peroxy radicals was observed.

When the reaction was carried out over the Sr-La₂O₃ catalyst the same benzyl radical spectrum as that shown in spectrum (a) was observed, but the amplitude was decreased by a factor of 2. The Sr-La₂O₃ sample became grey after 2 h use; whereas, the Li-MgO sample remained white, even after 6 h of reaction. The grey colour suggests that some of the benzyl radicals were converted to a carbonaceous material on the surface of Sr-La₂O₃ or that this material may have poisoned active centres on the catalyst.

The spectrum obtained over Sm₂O₃, shown in Fig. 1(c), was remarkably different from that obtained over the other two materials. The dominant four-line spectrum is that of CH₃· radicals. A smaller benzyl radical spectrum also is evident. The methyl radicals are believed to be formed by the homolytic cleavage of the C-C bond between the methyl group and the aromatic ring. In addition to the methyl radicals, one might expect to observe phenyl radicals, but there is no evidence for such radicals in spectrum (c). If they are formed, the phenyl radicals may react further on the surface, or in the gas phase, they may react with excess toluene to yield benzene and more benzyl radicals. The fact that Sm₂O₃ promotes the breaking of C-C bonds, rather than the abstraction of a hydrogen atom from the methyl group in toluene, is consistent with the observation by Kim *et al.*⁵ that this oxide is a rather nonselective cross-coupling catalyst. Carbon monoxide and carbon dioxide were the major products of the reaction.

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Fig. 1 ESR spectra of radicals from the reaction of toluene and nitrous oxide over catalysts: (a) experimental spectrum of benzyl radicals formed over Li-MgO; (b) simulated spectrum of benzyl radicals; (c) experimental spectrum of methyl and benzyl radicals formed over Sm₂O₃.

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