

Base-induced formation of nitrobenzene radical

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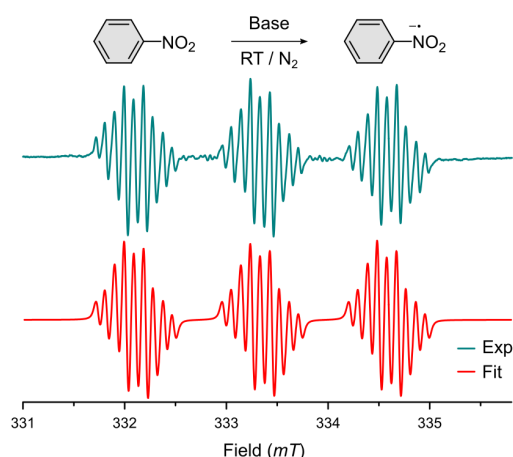
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Radical-containing nitroarenes afford non-conventional reaction pathways with a broad scope of applications. For instance, in synthesis, they have been inventively exploited for olefin dihydroxylation,^[1] hydrogen atom transfer^[2] or transannulation^[3] processes, while in biology they play a key role in the metabolic cycle of aerobic nitroreductases.^[4] Radical formation in nitroarene compounds occurs either electrochemically,^[5] by photoexcitation^[6] or via reaction with bases,^[7] but direct characterisation of the radical by means of electron paramagnetic resonance (EPR) is usually only possible in the former case, since the other procedures result in intermediate species. Thus, in our view, the method that yields structural and electronic information imposes conditions that are not the most suitable for more general syntheses. As such, we believe that studying whether nitroarenes radicals can be formed and characterized in simple conditions holds the potential to expand their transformative chemistry.

Here, building on previous studies,^[7] we report our first attempts to address this possibility. We study the simplest nitroarene, *i.e.*, nitrobenzene, in presence of different nucleophilic bases (*tert*-butyllithium, sodium *tert*-butoxide, sodium bis(trimethylsilyl)amide, sodium isopropyl cyclopentadiene) and solvents (tetrahydrofuran, benzene) in inert atmosphere. Room temperature X-band measurements confirm the formation of a nitro-based radical for all cases, which is stable until exposed to air. Density functional theory calculations indicate that the process is driven by a single electron transfer from the base to the nitrobenzene, but the oxidised base was not detected. To the best of our knowledge, this is the first-time nitrobenzene radical is generated by simple bases and characterised by EPR. Current efforts in the group focus on exploiting these stable radicals for novel synthetic procedures.



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