

Comment on "Formation of Nitroaromatic Compounds in Advanced Oxidation Processes: Photolysis versus Photocatalysis"

SIR: The recent paper by Dzengel et al. (1) is a valuable contribution to the knowledge on scope and limitations of advanced oxidation technologies for the cleanup of polluted groundwaters, surface waters, and process waters. The treatment of waters containing phenol(s) and nitrate can lead to the formation of nitrophenols. For the base case, with phenol and nitrate at pH = 5, the authors discuss possible mechanisms—centered on eqs 13 and 14 in their paper. The authors rejected a pathway via addition of OH to phenol followed by combination with NO₂ radical (their reaction 4b) on good grounds. We also note that this mechanism would result in the formation of 3-nitrophenol as a relatively important product, by OH addition at an ortho or para position, entrance of NO₂ next to this OH, and loss of water; however, this 3-isomer has not been observed. So, the authors state that "reaction 4b indeed can be neglected in comparison to reaction 13", meaning that the addition of a NO₂ radical to a phenol molecule is believed to be the real first step.

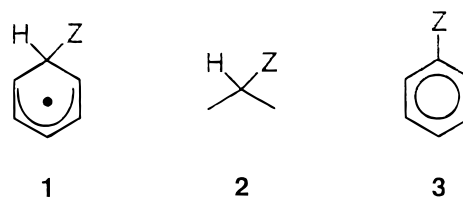
We wish to point out that this cannot possibly be true on thermochemical grounds. σ -bonding of a NO₂ radical to a benzene ring would imply a 'negative' C–N bond strength of at least ~ 10 kcal mol⁻¹.

This can be underscored by using known gas-phase thermochemical data (2, 3), as follows (Figure 1). For **1a**, the standard enthalpy of formation at 298 K, $\Delta_f H^\circ_{298}$, is 50 kcal mol⁻¹ (4). Common thermochemical approaches lead to a difference in $\Delta_f H^\circ_{298}$ between **2a** and **2b** of -8 kcal mol⁻¹, so one arrives at $\Delta_f H^\circ_{298}$ (**1b**) = 42 kcal mol⁻¹, 14 kcal mol⁻¹ above the sum of the values for benzene (**3a**, 20 kcal mol⁻¹) and NO₂ (8 kcal mol⁻¹).

Note that the mentioned value for $\Delta_f H^\circ_{298}$ (**1b**) implies a heat of addition for an H atom, $\Delta_f H^\circ_{298} = 52$ kcal mol⁻¹, to the ipso position in nitrobenzene (**3b**, $\Delta_f H^\circ_{298} = 16.5$ kcal mol⁻¹) of 26.5 kcal mol⁻¹ (as shown in Figure 2). Corresponding values for other Z range from around 18 (Z = F, NH₂, OH), via ca. 22 (Z = H, alkyl) to around 25 kcal mol⁻¹ for Z = Cl, Br, and I. Such differences can be understood on structural–chemical grounds (interaction of Z, especially in **3**, with the benzene ring).

Introducing a para-OH substituent in **3b** and in the corresponding **1b** certainly will bring some increase in the radical stabilization enthalpy of the latter (which amounts to ca. 21 kcal mol⁻¹ in the base case **1a**), but this will amount at most to 5 kcal mol⁻¹ (5). Hence, the addition of NO₂ to phenol shown in eq 13 of ref 1 will be at least ca. 9 kcal mol⁻¹ endothermal. Transfer from the gas phase to aqueous solution will not change much on thermochemical balances either. So, the thermochemistry of **1b** or its hydroxyl derivatives in aqueous solution will differ somewhat from the gas phase, but their formation—let alone with sufficient lifetime to allow bimolecular reaction with dissolved O₂—is to be excluded.

The question remains, then, how are nitrophenols really formed? Accepting that both phenoxyl radicals and NO₂ are present, we propose simply combination of these—with a rate constant near the diffusion limit—to make in first instance the keto forms of 2- or 4-nitrophenol. The corresponding C–N bond strengths will amount to roughly 45 and 40 kcal mol⁻¹, respectively (2). In this respect, the intermediate



a Z = H, b Z = NO₂

FIGURE 1. Chemical structures of 1–3.

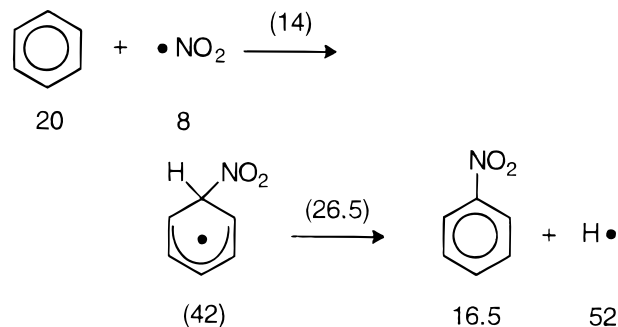


FIGURE 2. Thermochemistry of radical addition of NO₂ to benzene (numbers in parentheses are estimated values, in kcal mol⁻¹).

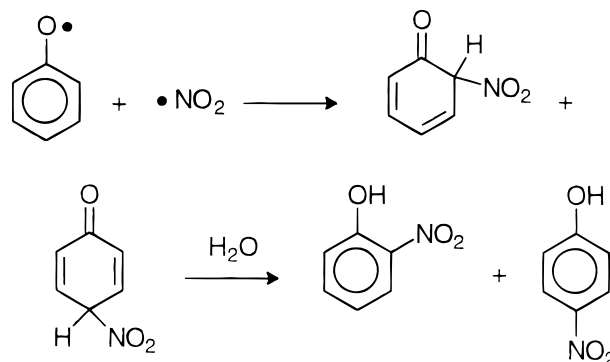


FIGURE 3. Proposed mechanism of formation of 2- and 4-nitrophenol.

products are long-lived; not so, of course with respect to *enolization* (by rapid proton transfers with water) giving 2- and 4-nitrophenol (Figure 3).

Literature Cited

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