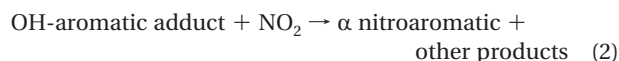


2008, Volume 42, Pages 9203–9209

Noriko Nishino, Janet Arey, and Roger Atkinson*: Formation of Nitro-Products from the Gas-Phase OH Radical-Initiated Reactions of Toluene, Naphthalene and Biphenyl: Effect of NO₂ Concentration

We previously studied formation of 3-nitrotoluene (3NT), 1- and 2-nitronaphthalene (1NN and 2NN), and 3-nitrobiphenyl (3NBiPh) from the OH radical-initiated reactions of toluene, naphthalene, and biphenyl over the range 0.014–4.2 ppmV of NO₂ (1). Nitroaromatic formation was interpreted using the following reactions:



Hence,

$$\text{yield of nitroaromatic} = \alpha k_2 [\text{NO}_2] / (k_2 [\text{NO}_2] + k_3 [\text{O}_2]) \quad (I)$$

where α is the nitroaromatic formation yield from reaction 2, and k_2 and k_3 are the rate constants for reactions 2 and 3, respectively. OH radicals were generated by the photolysis of CH₃ONO in air at ≥ 0.1 ppmV NO₂, and from the dark O₃ + 2-methyl-2-butene reaction at ≤ 0.2 ppmV NO₂. The experimental data at < 0.075 ppmV NO₂ and > 0.15 ppmV NO₂ were consistent with eq I with respective values of α and k_2/k_3 of 7.5% and 6.3×10^4 for 3NT formation, 0.35% and 3.6×10^6 for 1NN formation, 0.60% and 3.6×10^6 for 2NN formation, and 12% and 3.6×10^5 for 3NBiPh formation (1). However, as illustrated in Figure 1A for formation of 2NN from naphthalene (1), in the range 0.075–0.15 ppmV of NO₂ the yields of 1NN and 2NN from naphthalene and of 3NBiPh from biphenyl were up to a factor of ≥ 10 higher than predicted from eq I. Any increases in the formation yield of 3NT from toluene were much less significant (1). The increases in 1NN, 2NN and 3NBiPh were interpreted in terms of formation of NO₃ radicals and N₂O₅ at the lower initial CH₃ONO and NO concentrations when using CH₃ONO photolysis to generate OH radicals, and at the higher NO₂ concentrations when using the O₃ + 2-methyl-2-butene reaction to generate OH radicals. This enhanced formation of 3NBiPh was not due to reactions of NO₃ radicals with biphenyl, since in the presence of NO₃ radicals no loss of biphenyl nor formation of 3-nitrobiphenyl was observed (1). Furthermore, in the naphthalene reactions, the 1NN/2NN yield ratio under conditions where enhanced formation yields of 1NN and 2NN were observed remained close to that from the OH radical-initiated reaction (~ 0.6), in contrast to the 1NN/2NN yield ratio of ~ 2.2 from the NO₃ radical-initiated reaction of naphthalene (1). It was therefore proposed that the enhanced formation of 1NN, 2NN and 3NBiPh was likely due to reactions of the OH-aromatic adducts with N₂O₅ and/or NO₃ radicals (1).

To further investigate this effect, we have carried out additional experiments using both the O₃ + 2-methyl-2-butene and O₃ + 2,3-dimethyl-2-butene reactions to generate OH radicals in the presence of 0.05–1 ppmV of NO₂. 2,3-Dimethyl-2-butene reacts more rapidly than 2-methyl-2-butene with O₃ and NO₃ radicals, by factors of ~ 3 and ~ 6 , respectively (2), and hence NO₃ radical and N₂O₅ formation

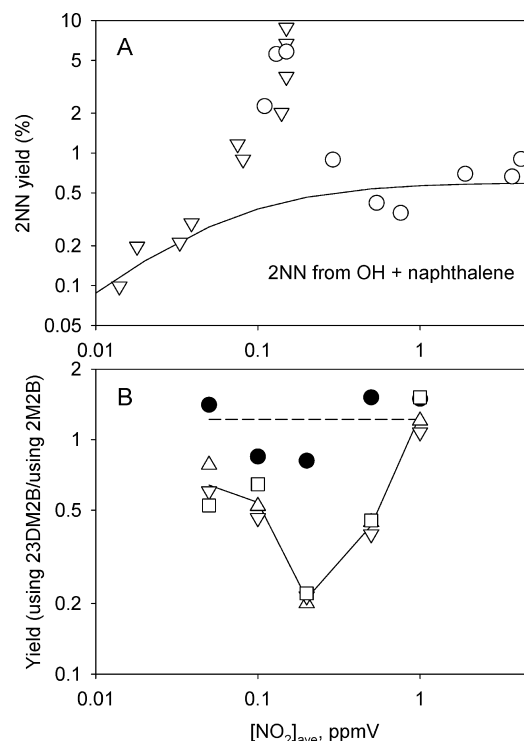


FIGURE 1. (A) Plot of previously measured (∇ , \circ) and predicted (—) 2-nitronaphthalene (2NN) formation yields from the OH radical-initiated reaction of naphthalene as a function of NO₂ concentration, using the dark O₃ + 2-methyl-2-butene reaction (∇) or photolysis of CH₃ONO (\circ) to generate OH radicals (1). (B) Ratios of the 3NT, 1NN, 2NN, and 3NBiPh yields measured in this series of experiments using 2,3-dimethyl-2-butene (23DM2B) compared to those when using 2-methyl-2-butene (2M2B) as the alkene. \bullet , 3NT; Δ , 1NN; ∇ , 2NN; and \square , 3NBiPh. The dashed and solid lines are for illustrative purposes.

should be significantly decreased when 2,3-dimethyl-2-butene is used instead of 2-methyl-2-butene. Using the same experimental methods as described previously (1), formation yields of 3NT from toluene, 1NN and 2NN from naphthalene and 3NBiPh from biphenyl were measured at 0.05–1 ppmV of NO₂. The resulting (nitroaromatic yield using 2,3-dimethyl-2-butene/nitroaromatic yield using 2-methyl-2-butene) ratios for formation of 3NT, 1NN, 2NN, and 3NBiPh are plotted against the NO₂ concentration in Figure 1B.

There was no significant difference between using 2,3-dimethyl-2-butene or 2-methyl-2-butene on formation of 3NT from toluene, consistent with our previous results (1). However, the formation yields of 1NN and 2NN from naphthalene and of 3NBiPh from biphenyl were a factor of ~ 4.5 – 5.0 lower at 0.2 ppmV NO₂ when using 2,3-dimethyl-2-butene instead of 2-methyl-2-butene (Figure 1B). Our new data are consistent with no enhanced nitroaromatic formation from either O₃ + alkene reaction at 0.05 ppmV NO₂, enhanced nitroaromatic formation when using the O₃ + 2-methyl-2-butene reaction at ≥ 0.1 ppmV NO₂, and enhanced nitroaromatic formation when using the O₃ + 2,3-dimethyl-2-butene at ≥ 0.2 ppmV NO₂. Hence, use of the more reactive (toward O₃ and NO₃ radicals) 2,3-dimethyl-2-butene delays artifactual nitroaromatic formation until the NO₂ mixing ratio is ~ 0.2 ppmV, versus ~ 0.1 ppmV when using 2-methyl-2-butene (1). These data suggest that the presence of NO₃ radicals and/or N₂O₅ is responsible for enhanced nitroaromatic formation from naphthalene and biphenyl, but as noted

above this is not due to NO_3 radical-initiated reactions. Rather, reaction of OH-aromatic adducts with species other than O_2 and NO_2 must occur, leading to order of magnitude more efficient nitroaromatic formation than from reaction 2.

Acknowledgments

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ES100917U

Qingzhu Zhang,* Shanjing Li, Xiaohui Qu, Xiangyan Shi, and Wenxing Wang*: A Quantum Mechanical Study on the Formation of PCDD/Fs from 2-Chlorophenol as Precursor

We noticed a mistake in Figure 1a on page 7303 of our paper published in *Environ. Sci. Technol.* **2008**, *42*, 7301–7308. This is the corrected Figure 1a:

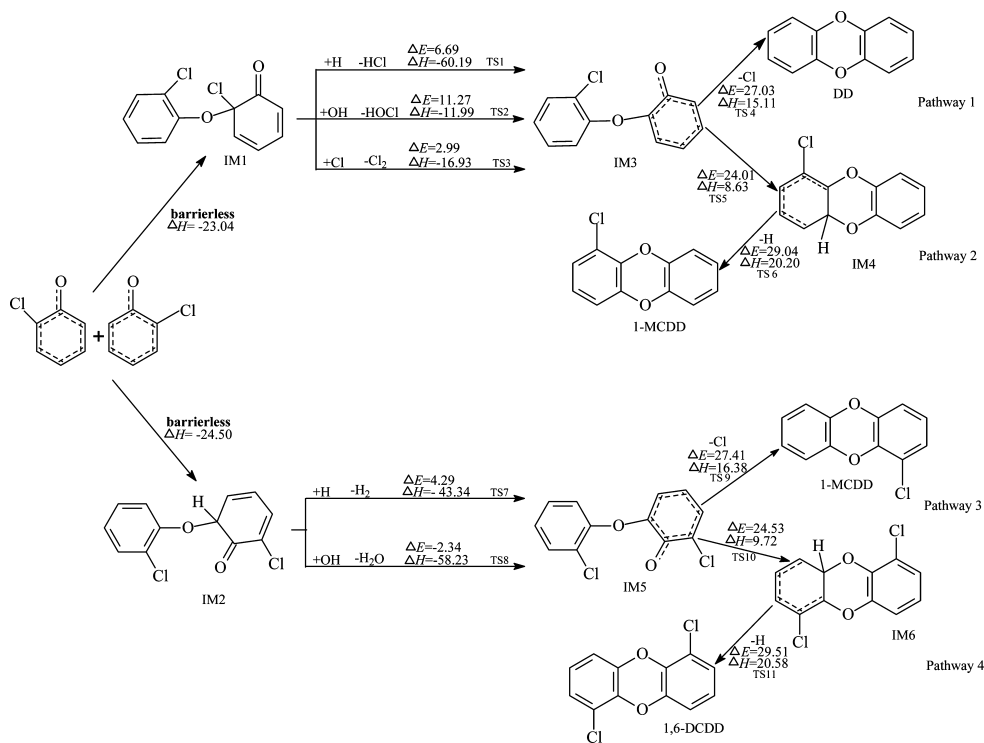


FIGURE 1a. Formation routes of PCDDs from the 2-CP precursor. ΔH is calculated at 0 K.

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