Relative roles of H-atom transfer and electron transfer in the debromination of polybrominated diphenyl ethers by palladized nanoscale zerovalent iron

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The relative significance of H-atom transfer versus electron transfer in the dehalogenation of halogenated organic compounds (HOCs) in bimetallic systems has long been debated. We have investigated this question through the case study of the debromination of 2, 2’, 4, 4’-tetrabromodiphenyl ether (BDE-47). The debromination rates of isomer products of BDE-47 by palladized nano zero-valent iron (n-ZVI/Pd) in the same reactor were compared. The results confirmed a shift in the debromination pathway of BDE-47 when treated with unpalladized nano zero-valent iron (n-ZVI) vs. treatment with n-ZVI/Pd. Study showed that BDEs could be rapidly debrominated in a palladium-H2 system, and the debromination pathway in this system is the same as that in the n-ZVI/Pd system. These results suggest that the H-atom species adsorbed on the surface of palladium are responsible for the enhanced reaction rates and the shift of the debromination pathway in the n-ZVI/Pd system. The Mulliken charges, calculated with density functional theory, on bromine atoms of PBDEs were directly correlated with the susceptibility to the e-transfer pathway in the n-ZVI system and inversely correlated with the susceptibility to the H-transfer pathway in n-ZVI/Pd system. These experimentally verified correlations in BDE-47 permit the prediction of the dominant debromination pathway in other BDEs.