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Comment on "Photodegradation Pathways of Nonabrominated Diphenyl Ethers, 2-Ethylhexyltetrabromobenzoate and Di(2-ethylhexyl)tetrabromophthalate: Identifying Potential Markers of Photodegradation"

In their article (1), Davis and Stapleton examine the photodegradation of nonabrominated diphenyl ethers (nonaBDEs), 2-ethylhexyltetrabromobenzoate (TBB), and di(2-ethylhexyl)tetrabromophthalate (TBPH). The authors provide an extended and generalized rationalization of the different rates of photodegradation for the nonaBDEs, as well as TBB and TBPH, in various organic solvents. The principles behind their discussions are incorrect, and require correction so the results of their study can be properly interpreted and integrated into the environmental photochemistry literature. After acknowledging that the mechanism of photoreductive debromination for nonaBDEs involves a "hydrogen atom donated from the solvent matrix", Davis and Stapleton then go on to discuss how "methanol is a very weak acid with an acid dissociation constant (pK_a) of about 15", and also state that "[t]he electron-withdrawing oxygen atom in the ring of THF may potentially increase the acidity of the protons on the ring; thus, it is conceivable that THF may be a better hydrogen donor than toluene, which lacks an electron withdrawing group and any obvious acidic protons." (1) The authors have confused proton transfer (proton donor) with hydrogen atom transfer (hydrogen atom donor). These processes are not related for the mechanisms under question, and by this discussion (and a similar discussion regarding the photodegradation of TBB and TBPH), the authors are overlooking basic and well-established principles of organic chemistry (2).

For reductive photodebromination of BDEs in hydrocarbon solvents such as methanol, THF, and toluene, there is first a photochemical homolytic aryl-bromine bond cleavage to yield an aryl radical and its bromine radical counterpart, which then either recombine within the solvent cage to yield no net reaction, or each subsequently abstract a hydrogen atom via ground state reactions from the organic solvent to give the photoreductively debrominated BDEs and HBr as primary photoproducts (3). The relative ease with which the aryl radical can abstract a hydrogen atom from the solvent is related to the weakest ground state bond dissociation enthalpy (BDE) for the solvent, not its pK_a . In the case of methanol, the $H-CH_2OH$ bond is considerably weaker (96 kcal mol^{-1}) than the CH_3O-H bond ($105 \text{ kcal mol}^{-1}$) (4). Thus, it is not the alcoholic hydrogen which is abstracted, but the alkyl hydrogen. Acidity is not related to hydrogen atom transfer, otherwise water, being more acidic than methanol, would be an excellent hydrogen donor. Water is not a good hydrogen atom donor, of course, having an $O-H$ homolytic BDE of $119 \text{ kcal mol}^{-1}$ that is much higher than BDEs for the $C-H$ bonds in most hydrocarbons (which range from about 90 to $100 \text{ kcal mol}^{-1}$). THF has a BDE of about 92 kcal mol^{-1} (5). The benzylic hydrogen on toluene has an unusually low BDE of 90 kcal mol^{-1} (4), a value much lower than for any of the ring hydrogens (BDEs of about 113 kcal

mol^{-1}), due to the resonance stabilization of the resulting benzylic radical. Thus, when Davis and Stapleton report that the "nonaBDEs degraded fastest in toluene and at approximately the same rate in methanol as in THF", and then go on to claim that the "hydrogen donation capabilities of the solvent do not fully explain the photodegradation kinetics of nonaBDEs" (1), they are wrong. Toluene is well-known among the mechanistic organic photochemistry community as a better hydrogen atom donating solvent than THF or methanol. The photoreductive debromination kinetic results of Davis and Stapleton for nonaBDEs (1) are fully consistent with the known hydrogen atom donation capabilities of these three solvents, and do not require the erroneous ground or excited state acidity-based analyses the authors put forward.

The authors go on to propose an indirect photolysis mechanism involving photochemistry of the three solvents under their solar irradiation conditions for nonaBDEs, TBB, and TBPH. Solutions of pure methanol, THF, or toluene neither absorb any significant quantities of radiation at the solar wavelengths being used, nor undergo any significant photochemistry (6) that could participate in the "indirect photodegradation" of nonaBDEs, TBB, and TBPH that Davis and Stapleton hypothesize. Consequently, the reported photoreactivities of all materials (including TBB and TBPH) reported by Davis and Stapleton under their experimental conditions are due to the direct photolysis of these compounds, rather than indirect photolytic discussions these authors incorrectly put forward.

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