Free-Radical Bromination of Selected Organic Compounds in Water

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Environmental consideration prompts an urgent need to redesign commercially important chemical processes and products or to invent new ones that make use of chemicals that are less toxic and more environmentally benign.[1] Water could also be used as a substitute solvent for free-radical bromination. Like supercritical carbon dioxide,[2] it is nontoxic and environmentally benign. Water is an excellent medium for free-radical reactions because its OH bond is remarkably strong,[3] so hydrogen abstraction from the solvent is unlikely. It does not possess reactive multiple bonds to which radicals might add. Indeed, in the field of pulse radiolysis, reactions are normally carried out in water.[4−7] The potential problems with water as the medium for radical reactions relate to the limited solubility of most organic materials and its high polarity, which could influence the course of the bromination. In this work, we report on the free-radical bromination of some simple hydrocarbons in water. Also, for two representative compounds we ran the bromination neat, i.e., without any solvent, to ascertain the role of water in the reaction.

The following organic compounds, *o*-xylene (**1**), toluene (**2**), *p*-xylene (**3**), *m*-xylene (**4**), diphenylmethane (**5**), triphenylmethane (**6**), mesitylene (**7**), durene (**8**), cyclohexane (**9**), and cyclohexene (**10**), have been used as the organic starting materials in the free-radical bromination reactions in water. Since Br_2 shows significant absorption of light in the visible region, $\lambda_{max} \approx 415$ nm,[8] the reaction was initiated photolytically using an ordinary incandescent light bulb.

The absorbed light intensity (photon flux) from the incandescent light bulb was also measured with the aid of potassium ferric oxalate solutions in a method developed by Hatchard and Parker,[8] and the average value was calculated to be 7.31×10^{15} quanta/s of absorbed radiation. It was observed that due to the proximity of the light bulb (~5 cm distance) to the flask, the reaction temperature rose to ~80 °C. The free-radical bromination was shown not to be brought about thermally by running dark controls at 80 °C and at room temperature for a period of several days. In all of these experiments, *o*-xylene (**1**) was used as organic starting material being brominated. In water, photobromination of *o*-xylene (**1**) afforded predominantly side-chain bromination products, whereas in the dark, exclusively ring bromination occurred (Table 1).

In water, the photobromination reactions of toluene (**2**), *p*-xylene (**3**), *m*-xylene (**4**), diphenylmethane (**5**), and triphenylmethane (**6**) produced the corresponding side-chain bromination products in high yields (see Table 2). In all of these alkylaromatics, the corresponding ring bromination products were produced in trace amounts. Also, all of these photobrominations evinced an interesting partitioning of organics, the unbrominated reactant residing *on top* of the middle layer that containined the unreacted aqueous HBr and the brominated products forming a lower, heavier than water layer.

On the other hand, in water, the bromination of mesitylene (**7**) and durene (**8**) either in the presence or absence of light, produced solely ring bromination products (see Table 3). In CCl_4, bromination of mesitylene (**7**), a highly nucleophilic aromatic compound that produces 2-bromomesitylene, could be done either in the dark or with light.[9]

The photobromination of cyclohexane (**9**) in water (see Table 4) was complete in a few minutes, giving monobromocyclohexane and vicinal dibromocyclohexane, with the same three-phase partitioning effect that was observed with the alkylaromatics. No reaction occurred in the dark.

The bromination of cyclohexene (**10**) in water either in the presence or absence of light produced *trans*-1,2-dibromocyclohexane as the only product; no free-radical, allylic bromination occurred (see Table 5).

To ascertain the role water plays in this free radical system, we ran the photo bromination of toluene (**2**) and cyclohexane (**9**) *neat*, i.e., without any water. As Tables 6 and 7 show, product yields were comparable to reactions run in the presence of water.

It thus seems likely that (a) in the presence of water, the reaction takes place in the *organic* phase and (b) water exerts no significant effect on the bromination *itself*.[10] Nevertheless, water serves a number of important functions: (1) The coproduct HBr is efficiently scavenged, while in the neat reaction, HBr escapes untrapped. (2) By providing a diluting medium, free radicals are uniformly distributed over the reaction volume. Thus, recombinations are minimized near the window where the radiation is entering the reactor. (3) The diluting medium also promotes uniform reaction temperature, which helps obtain better product distribution. (4) An interesting and potentially more important feature of water-based reactions is the property of water to *partition* the heavier-than-water bromination reaction product from the lighter-than-water starting materials. All free-radical brominations gave reaction mixtures consisting of three layers: a lower organic layer analyzed for reaction product(s), a middle aqueous layer titrated for the stoichiometric amount of HBr, and an upper organic layer that was analyzed for starting material.

This partitioning phenomena, which can be generalized to most brominations, will dramatically simplify reaction workup and product isolation procedures, compared to reactions run neat or in CCl_4.

Our results show that aliphatic and alkyl-substituted aromatic substrates that are not highly nucleophilic with

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[1] Illmann, D. *Chem. Eng. News* **1994**, *72*, 22.

[2] Tanko, J.; Blackert, J. *Science* **1994**, *263*, 203.

[3] Morrison, R.; Boyd, R. *Organic Chemistry*, 5th ed.; Allyn and Bacon, Inc.: Boston, 1987; p 22.

[4] Lind, J.; Jonsson, M.; Erikson, T. *J. Phys. Chem.* **1993**, *97*, 1610.

[5] Gabor, M.; Lind, J. *J. Am. Chem. Soc.* **1994**, *116*, 7872.

[6] Zhang, X.; Zhang, N.; Schuchmann, H. *J. Phys. Chem.* **1994**, *98*, 6541.

[7] Domae, M.; Katsumara, Y.; Jiang, P. *J. Phys. Chem.* **1994**, *98*, 190.

[8] Calvert, J.; Pitts, J. *Photochemistry*; John Wiley: New York, 1966; p 783.

[9] Smith, L. In *Organic Synthesis*; Blatt, A., Ed.; John Wiley: New York, 1943; Collect. Vol. II, p 94.

[10] We acknowledge with gratitude one of the reviewers for incisive comments and suggestions regarding the function of water.

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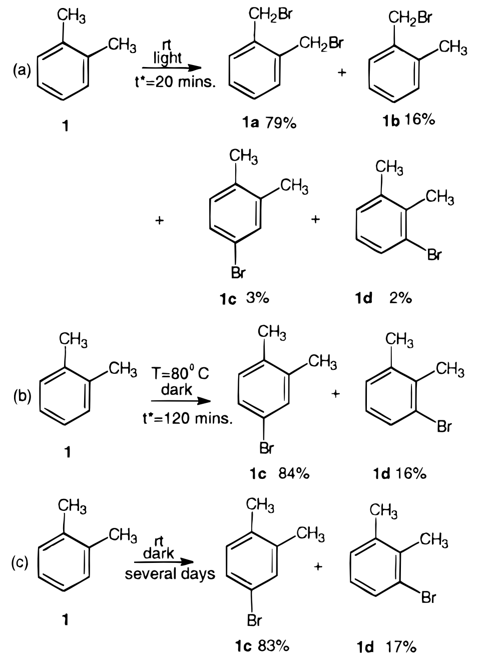
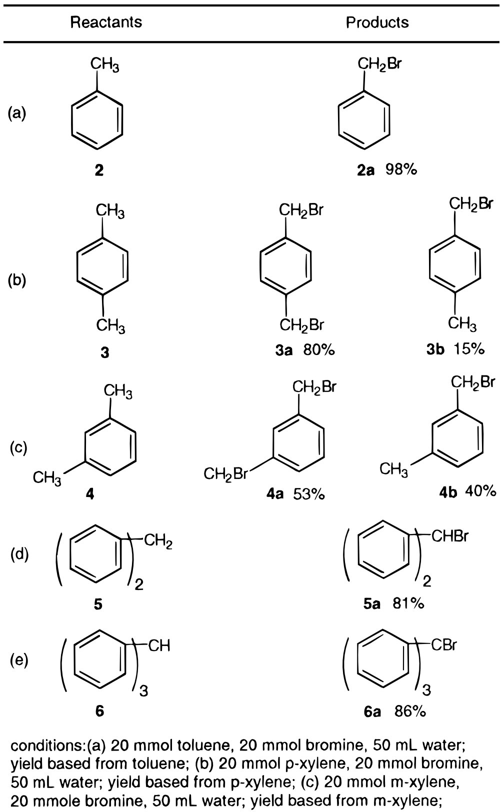
Table 1. Products and Yields of Bromination of *o*-Xylene (1) in Water



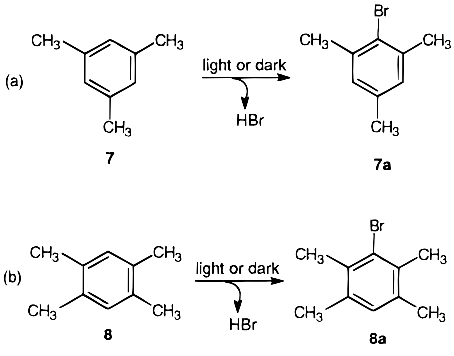
*time of disappearance of bromine color; conditions: 10 mmol 1, 10 mmol bromine, 25 mL water; yields determined by GLC analyses using DB-WAX capillary column with oven temperature programming, 60-200° C, and with the use of external standards.

Table 2. Products and Yields of Photobromination of Some Alkylaromatics in Water



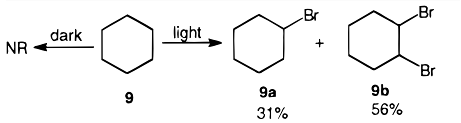
conditions: (a) 20 mmol toluene, 20 mmol bromine, 50 mL water; yield based from toluene; (b) 20 mmol p-xylene, 20 mmol bromine, 50 mL water; yield based from p-xylene; (c) 20 mmol m-xylene, 20 mmole bromine, 50 mL water; yield based from m-xylene; (d) 10 mmol diphenylmthane, 10 mmol bromine, 25 mL water; (e) 10 mmol triphenylmethane, 10 mmol bromine, 25 mL water; for (d) and (e), yields were determined by GLC analyses using Tenax stainless steel packed column with oven T=300 °C and with the use of external standards

Table 3. Products of Bromination of Mesitylene (7) and Durene (8) in Water



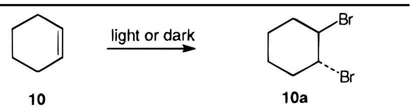
conditions: (a) 20 mmol **7**, 10 mmol bromine, 50 mL water; (b) 20 mmol **8**, 10 mmol bromine, 50 mL water.

Table 4. Products and Yields of Bromination of Cyclohexane (9) in Water



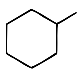
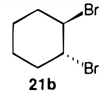
conditions: 10 mmol **9**, 10 mmol bromine, 25 mL water; yields determined by GLC analyses using 5% SE-30 on Chrom Q packed column with oven temperature programming, 60-120°C and using external standards.

Table 5. Product of Bromination of Cyclohexene (10) in Water



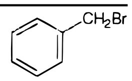
condition: 20 mmol **10**, 20 mmol bromine, 25 mL water; stereochemistry of product based from comparison of its proton NMR spectra with the proton NMR spectra of commercially available trans-1,2-dibromocyclohexane.

Table 6. Bromination of Cyclohexane (9): Neat, vs H_2O

Entry	Conditions	 **21a**	 **21b**
1	$Br_2 / h\nu$	35	13
2	$Br_2 / H_2O / h\nu$	33	23

For reaction conditions & GC-FID analysis see: Supplementary materials

Table 7. Bromination of Toluene (2): Neat, vs H_2O

Entry	Conditions	
1	$Br_2 / h\nu$	95
2	$Br_2 / H_2O / h\nu$	98

For reaction conditions see: Supplementary materials

respect to Br_2 in polar media will yield easily isolable free-radical substitution products in aqueous media under irradiation. However, highly nucleophilic compounds such as mesitylene, durene, and cyclohexene all undergo ionic ring substitution or addition in H_2O even in the presence of light. Nevertheless, we feel that we have opened the door to a wide spectrum of free-radical brominations that can be performed in the absence of toxic solvents such as CCl_4.

Supporting Information Available: Typical experimental procedures and analytical results in the bromination of alkanes and aromatic alkanes in water are available (8 pages).

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