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Quaternary Ammonium Salts as Bifunctional Catalysts in the Oxybromination of Aromatic Compounds by Aqueous Hydrogen Bromide/Hydrogen Peroxide

Jihad Dakka and Yoel Sasson*

Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Quaternary ammonium salts function both as Lewis acids and as phase-transfer catalysts in the bromination of aromatic compounds in the presence of hydrogen peroxide.

The classical direct halogenation (chlorination or bromination) of aromatic systems suffers from being wasteful in the halogen employed: one half ends up as hydrogen halide. In large-scale operations this is an environmental as well as an economic problem. A possible solution is the oxidation and recycling of the by-product HCl or HBr. It is particularly convenient to apply an *in situ* oxidizing agent, resulting in a one-pot synthesis. In this respect hydrogen peroxide is the reagent of choice being cheap and selective and forming no side products except water.[1] This method was demonstrated in the oxyhalogenation of olefins.[2]

A typical oxybromination of an aromatic compound in the presence of hydrogen peroxide proceeds according to the stoicheiometry of equation (1). Oxybrominations of this type are very useful for active aromatic systems which do not require the presence of a Lewis acid catalyst for the bromination step, such as phenols or anilines.[3] However, reaction (1) cannot be applied to the bromination of unactivated aromatic derivatives, where catalysts like aluminium chloride or ferric chloride are needed, simply because these catalysts are inactive in aqueous medium.

$$2ArH + Br_2 + H_2O_2 \rightarrow 2ArBr + 2H_2O \qquad (1)$$

We have now found that oxybrominations of benzene, toluene, ethylbenzene, and chlorobenzene proceed effectively according to equation (1) if catalytic amounts of quaternary ammonium salts are present. The catalysts in these biphasic systems perform a dual function: normal Lewis acid catalysis and phase-transfer catalysis for the extraction of both hydrogen peroxide and hydrogen bromide into the organic phase.

In a typical example, bromine (1 mol) was added dropwise to a stirred mixture of benzene (2 mol), aqueous 30% hydrogen peroxide (1 mol) and tetra-n-butylammonium bromide (TBAB) (0.1 mol) over 4 h while the mixture was kept at a constant temperature of 65 °C. Stirring was continued at this temperature for an additional 8 h. After cooling, the organic phase was separated, dried over magnesium sulphate, and distilled to yield bromobenzene (1.85 mol, 92.5%).

Alternatively, the bromine source in the oxybromination can be aqueous hydrobromic acid. In this case the stoicheiometry is that of equation (2). In a typical example hydrogen peroxide (1.1 mol) was slowly added over 4 h to a mixture of benzene (1 mol), 50% hydrobromic acid (1.2 mol) and TBAB (0.1 mol) at 65 °C. After cooling and separation of the organic phase, 90% of the theoretical yield of bromobenzene was recovered by distillation.

$$HBr + H_2O_2 + ArH \rightarrow ArBr + 2H_2O \qquad (2)$$

A similar procedure was applied for the oxychlorination of benzene except that a larger excess of concentrated hydrochloric acid was required for high conversion. Thus 30% hydrogen peroxide (1.1 mol) was added during 2 h to a mixture of benzene (0.1 mol), 32% hydrochloric acid (6.0 mol) and TBAB (0.1 mol) at 65 °C. After phase separation 0.95 mol of chlorobenzene was obtained by distillation.

Alkylbenzenes reacted similarly in brominations, oxybrominations, and oxychlorinations. In general, the *ortho-para* isomer distribution was much the same as in iron-chloride-catalysed halogenation.

Several rate measurements were made in order to clarify the mechanism of these reactions. In these experiments all the reactants were mixed at constant temperature and samples were taken at intervals both from the organic phase and, when present, from the aqueous phase. Analysis was performed by gas chromatography (organic phase) and by potentiometric titration (aqueous phase). The following observations were made. (*a*) Quaternary ammonium salts catalyse the reaction of elementary bromine with the aromatic ring. Bromination of benzene was 50—70 times slower in the absence of the catalyst. (*b*) The catalytic activity of different quaternary ammonium bromide salts in the bromination step decreases in the order: tetraethyl > tetrapropyl > tetrabutyl > tetrahexyl > tetraoctyl > tetramethyl. This order of decreasing activity was also found in the presence of hydrogen peroxide. Application of quaternary salts with different anions, *e.g.* chlorides or hydrogen sulphates, did not alter the reaction rate as compared with those of the corresponding bromides. (*c*)

The catalytic activity of the quaternary ammonium bromides was enhanced by the presence of hydrobromic acid. Thus reaction of benzene with bromine in the presence of TBAB was four times slower when 1 equiv. of sodium carbonate was initially present in the mixture, neutralizing the HBr released. (*d*) Oxidation of hydrobromic acid to bromine by hydrogen peroxide, in the presence of an inert organic phase (*e.g.* dichloromethane) was twice as fast when 5 mol % of TBAB was added.

These results clearly indicate that the bromine molecule is activated by the quaternary ammonium salt for electrophilic attack on the aromatic ring. This may well be achieved by the formation of adducts of general structure R_4NBr_n ($n = 3$ or 5) in which the bromine molecules are partially polarized. The polarization of the complexed bromine is stronger with smaller quaternary cations, owing to the proximity of the bromine molecule to the charged nitrogen. This type of adduct is known to function as a mild brominating agent.[4] The exceptional behaviour of the tetramethylammonium catalyst is due to its very low solubility in the reaction medium.

In the presence of hydrogen bromide it is probable that a different adduct with the general structure $R_4NBr{\cdot}HBr$ is initially formed. This species forms another type of complex with bromine, probably with structure $R_4NBr{\cdot}HBr_n$. The complex would be expected to be a stronger aromatic bromination agent because polarization of the complexed bromine is induced both by the charged nitrogen and by the proton. A similar co-catalysis by protic acids is well known in Friedel-Crafts reactions in the presence of the Lewis acids.[5] That this adduct cannot be formed in the presence of a base explains the retarding effect of carbonate on the bromination.

Thus quaternary ammonium salts act as multifunctional catalysts in the oxybromination of aromatic hydrocarbons in the presence of hydrogen peroxide.

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