

The electrophilic bromination of olefins with amine-bromine complexes and quaternary ammonium tribromides

Giuseppe Bellucci

The bromination of olefins with molecular Br_2 has been the object of very extensive investigation. Bromination with Br_2 complexes, like the 1 : 1 pyridine- Br_2 complex (PyBr_2) and quaternary ammonium tribromides, has received much less attention, in spite of the advantage of using these stable and easily handled solids in place of the free halogen.

An attractive feature of these brominating reagents is their ability to give stereoselective and, by using appropriate chiral organic moieties, enantioselective additions to alkenes. Bromination of alkenes in the presence of Chinchona alkaloids produces optically active dibromides of low optical purity, probably through the reaction of a chiral alkaloid- Br_2 complex formed *in situ*. The use of PyBr_2 in place of free Br_2 increases the diaxial to diequatorial dibromide ratio obtained from cyclohexene derivatives and favours anti addition against syn addition and proton loss from intermediate bromocarbonium ions in the bromination of aryl substituted olefins. PyBr_2 and tribromide salts react with conjugated dienes to give much higher ratios of 1,2 to 1,4 and of anti to syn dibromo adducts than free Br_2 .

Detailed information on the mechanism of olefin bromination in the presence of pyridine has been obtained by kinetic and product studies in chlorinated hydrocarbon solvents. These studies have revealed a complex reaction sequence, leading to dibromo adducts and to pyridine incorporation in N-(2-bromoalkyl) pyridinium bromides which capture Br_2 to give the corresponding tribromides. The bromination is thus carried out by the competition of three distinct electrophiles in equilibrium, Br_2 , PyBr_2 and Br_3^- , and the latter two species are responsible for the changes in products with respect to the reactions of molecular Br_2 .

Aliphatic amines are not suitable for use in bromination since their complexes with Br_2 , even when endowed with a very high formation constant as in the case of $\text{Et}_3\text{N}-\text{Br}_2$ ($K_f > 10^7 \text{ M}^{-1}$ in 1,2-dichloroethane), undergo a fast intramolecular oxidation-

reduction consuming the halogen.

Mechanistic information concerning the reactions of molecular bromine and of tribromide ion has been achieved by a comparative kinetic and product investigation of the bromination of cyclohexene derivatives with the free halogen and with tetrabutylammonium tribromide in chlorinated hydrocarbon solvents. The two reactions exhibit different kinetic orders (second-order in Br_2 , first-order in Br_3^-), with rates showing opposite temperature coefficients (negative for Br_2 , positive for Br_3^-). The rate constant is substantially determined by the solvent polarity, with a linear dependence of $\ln k$ against the Kirkwood function of the dielectric constant, for the Br_2 but not for the Br_3^- reactions. The Br_3^- reaction, but not the Br_2 addition, is subjected to a kinetic solvent isotope effect in $\text{CHCl}_3/\text{CDCl}_3$. Steric factors exert larger retarding effects on the Br_3^- than on the Br_2 additions, while inductive effects of electronwithdrawing substituents retard the Br_2 much more than the Br_3^- reactions. The products of the addition of molecular Br_2 to cyclohexene derivatives consist of mixtures of diaxial and diequatorial dibromo adducts in ratios depending on the substituents. 3-Benzoyloxy-substituted cyclohexenes give also cis-1,2- and cis-1,3-dibromides, formed by collapse of 2-phenyl-1,3-dioxolan-2-ylum tribromide salts arising from the first formed bromonium-tribromide ion pair intermediates. Only diaxial and diequatorial 1,2-dibromo adducts, with a large prevalence of the former, are instead always obtained in the Br_3^- reactions. The kinetic and product results indicate for these Br_3^- reactions a rate- and product-determining nucleophilic attack by Br on olefin- Br_2 charge transfer complexes in equilibrium with the olefin and Br_3^- .

Asymmetric induction higher than that achieved in bromination with Chinchona alkaloids has been obtained in the bromination of cyclohexene using tribromide salts of optically active quaternary ammonium ions in apolar solvents.