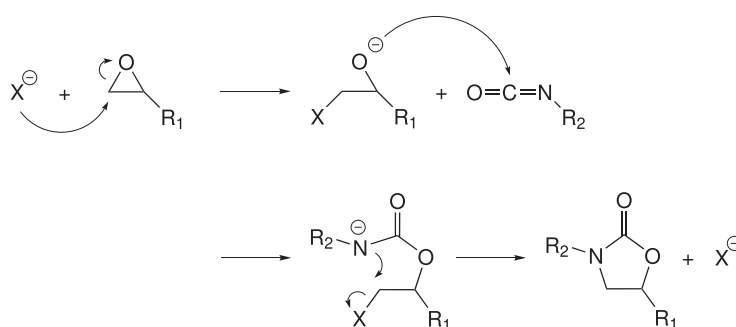


3.2.6 Oxazolidinone formation

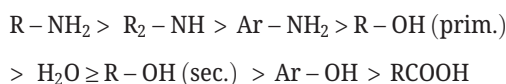
Oxazolidinone (oxazolidin-2-one) can be formed in the stoichiometric reaction of an epoxide with an isocyanate. The pathway of the three-step reaction leading to oxazolidinone involves the epoxide opening through a nucleophilic attack by an anionic species, followed by the attack of the formed alkoxide on the central carbon atom of the isocyanate. A final ring closure leads to the oxazolidinone through an internal attack of the anionic nitrogen atom on the carbon atom binding the initiating nucleophile. The nucleophile, for example a halide, is liberated upon ring closure.

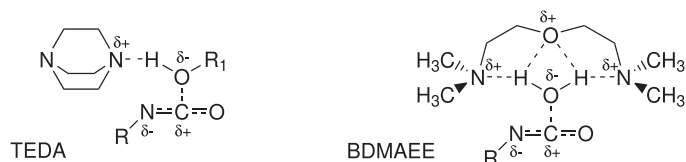


Efforts were made to find catalyst systems for the selective formation of oxazolidinones. Phosphonium and ammonium halides, such as tetraphenylphosphonium and tetrabutylammonium chloride and bromide, are highly selective catalysts at temperatures of approximately 180 °C. The reaction of bisphenol diglycidyl ether and 2,4-TDI or 4,4'-MDI in the presence of these catalysts yielded linear, high-molar-mass polymers [5]. The thermal stability of oxazolidinones is between that of urethane and isocyanurate.

3.2.7 Reactivity and catalysis

During polyurethane formation, the reactions with the various active hydrogen components and isocyanate will proceed in parallel but with different reaction rates. Amines react faster than alcohols, which, in turn, react faster than carboxylic acids. This shows that the nucleophilicity of the reactive group is more important than its acidity. Furthermore, steric hindrance on the reactive group will reduce its reactivity. Primary alcohols react faster than secondary alcohols, and likewise for amines. The following ranking for amines, alcohols, water, and carboxylic acids is generally accepted (R and Ar stand for aliphatic and aromatic, respectively) [2]:





Bis(2-dimethylaminoethyl) ether (BDMAEE) is an excellent catalyst for the isocyanate-water reaction. Its structure – a symmetrical molecule containing three hetero atoms spaced by two carbon atoms – allows the formation of stable hydrogen bonds with water through multiple bonding interactions. The strong hydrogen bonding increases the charge density of the water oxygen atom, which facilitates its nucleophilic attack on the isocyanate. This multi-cryptand hydrogen bonding interaction does not occur with hydroxyl groups; instead, urethane catalysis occurs through a straightforward acid-base interaction between the amine and hydroxyl group, as discussed previously. The central oxygen atom, however, withdraws charge from the terminal nitrogen atoms, reducing their basicity – the pKa values of the two amines are 9.6 and 7.9. The reduced basicity of the amines decreases their ability to catalyze the urethane reaction. Consequently, BDMAEE possesses a much stronger catalytic activity for the water-isocyanate reaction than for the urethane reaction.

The differences in urethane-to-urea catalyzing properties of the various catalysts used in the industry can be expressed by their “gel-to-blow” ratio [7]. This factor is 20:80 for BDMAEE, whereas it is 88:12 for TEDA. These two catalysts represent the extremes regarding the blow-to-gel activity of commercially available tertiary amine catalysts. DMCHA, for example, has a gel-to-blow ratio of 73:27.

Organic tin compounds are the most generally employed Lewis acid catalysts. These catalysts show high reactivity and specificity toward the urethane reaction. Di-butyltin dilaurate (DBTDL), for instance, exhibits a gel-to-blow ratio of 97:3. The gel-to-blow ratios of DBTDL, TEDA, DMCHA, and BDMAEE are graphically illustrated in Fig. 3.1.

Catalysts are essential ingredients in PU formulations. Catalytic reactivity and chemical selectivity are important parameters when selecting the catalyst. The former

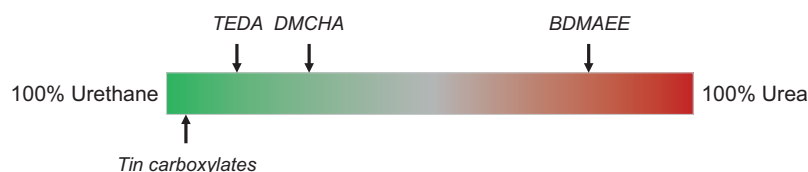


Fig. 3.1: Gel-to-blow ratios of some standard polyurethane catalysts.