Abstract: We studied computationally, on the model compound ethylenediamine, the insertion of carbon dioxide into diamines, yielding cyclic urea compounds. Two mechanisms were elaborated, depending on the value of the dielectric constant (DC) of the solvent. Accordingly, reaction mixtures with a high DC lead to carbamates, whereas lower DC values result in the preferred product cyclic urea. Additives behaving as proton shuttles act as catalysts, significantly reducing the activation barriers of insertion and ring closure to surmountable values. CO2 insertion into diamines may also occur by autocatalysis, even without further additives, but under less favorable conditions, for example, lower yields. Amine reagents are most efficient at proton shuttling, followed by alcohols. The activation barrier of the rate-limiting step is lowered in a reaction mixture with higher values of DC, up to a critical value ecｒ similar to 18. Hence, in a suitably optimized reaction mixture, ring closure is suggested to occur under milder conditions than those previously applied experimentally. The two roles of the additive, that is, acting as proton shuttling agent and adjusting the effective DC of the reaction mixture, do not have to be assigned to a single compound, possibly affording a handle on process optimization.
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