Water: the Solvent of Choice

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Miscibility not required: chemical reactions "on water" faster than in organic solvents

We all know what it means to put something "on ice", but what is a chemical reaction "on water"? This new expression has been coined by a team headed by K. Barry Sharpless, winner of the 2001 Nobel Prize for chemistry, to describe reactions of organic substances that are not water-soluble, yet react well or even considerably faster in the presence of water than in organic solvents. If water could also replace organic solvents more often on the industrial scale, it would save money, increase the safety of chemical facilities, and reduce stress on the environment. Another advantage is that after the reaction, the organic and aqueous phases separate, eliminating the need for complex isolation steps to obtain the product.

Until now, a central aspect in the area of aqueous organic chemistry has been the effort to improve the water- solubility of the substances involved. Has this been the wrong approach? Is the axiom that has been passed on from the days of alchemy, corpora non agunt nisi soluta (substances do not interact with each other if they are not dissolved), no longer valid? Do reactants not need to be water-soluble at all in order to react in an aqueous environment? It seems that the situation bears some rethinking. Says Sharpless, "In contrast to prior assumptions, it seems that in many cases the immiscibility of the organic and aqueous phases is a considerable advantage."

So what exactly does "on water" mean? The expression simply refers to the fact that the reactants and the water are vigorously stirred together. This forms a suspension, meaning that the immiscible liquids are finely divided into tiny drops. The contact surface between the aqueous and organic phases is thus especially large.

Why certain important categories of reactions, such as the Claisen rearrangement, work so well in aqueous suspension is not yet clear. Particularly astonishing is the fact that the reactions occasionally go faster "on water" than in a mixture of the pure reactants (without any solvent). "Molecules at the interface between two different phases often behave differently than molecules within the phase." Sharpless speculates: "It is possible that the unique properties of molecules at the interface between the water and the hydrophobic, oily organic phase play an important role in speeding up the reactions."

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