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Photoisomerisation of trans-stilbene in solution may be directly assisted by solvent collisions

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Gas phase thermal isomerization rates of trans-stilbene obey the Arrhenius law at $T \sim 300$ K, indicating that intramolecular vibrational redistribution (IVR) is complete or not restrictive for the reaction. In solution the rates increase ten-fold and become nearly independent on intramolecular temperature (or excitation wavelength). These observations are difficult to express through RRKM theory. Mechanisms suggested so far, like restricted IVR, nonadiabaticity, or solvent-dependent barriers, may explain only the increase in the rates but not the wavelength independence. We propose that solute-solvent collisions directly promote isomerization, in addition to intramolecular activation. The two activation mechanisms can be experimentally distinguished by the weak dependence on excitation wavelength.

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