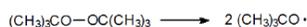


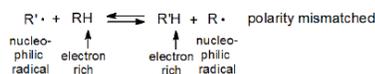


Scheme 2

initiation phase



propagation phase


 $\text{R}\cdot$  = a radical derived from a carbohydrate acetal by hydrogen abstraction

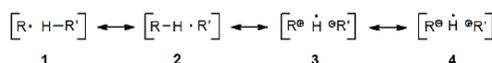
 $\text{R}'\cdot$  = a radical produced from  $\text{R}\cdot$  by ring opening,  $\beta$ -fragmentation, or ring inversion


Figure 1. Valence-bond structures describing the transition-state for hydrogen abstraction

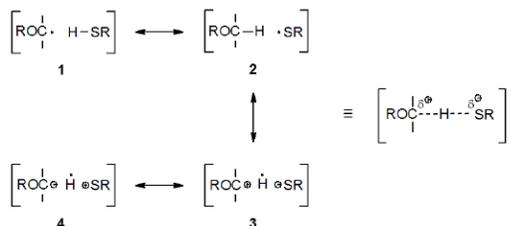


Figure 2. Representations for the transition state in hydrogen-atom transfer between carbon and sulfur atoms

A structure such as **3** is a transition-state-stabilizing contributor in any hydrogen-abstraction reaction where a change in radical philicity takes place. Such a change occurs in propagation steps 1 and 3 in the thiol-catalyzed mechanism pictured in [Scheme 1](#), but it does not take place at all in the uncatalyzed mechanism shown in [Scheme 2](#). When a change in radical philicity occurs during a reaction, either due to abstraction of an electron-rich hydrogen atom by an electrophilic radical or abstraction of an electron-deficient hydrogen atom by a nucleophilic radical (propagation steps 1 and 3, respectively, in Scheme 1), the reaction is described as polarity-matched.<sup>4,10</sup> If one radical must be converted into another by hydrogen-atom abstraction without benefit from a change in radical philicity (step 2 in Scheme 2), the reaction is described as being polarity-mismatched. The transition state for a polarity-matched reaction will be stabilized by contribution from the charge-separated, valence-bond structure **3** (Figures 1 and 2), but a polarity-mismatched reaction will not experience similar, transition-state stabilization. A polarity-matched reaction, therefore, will have transition-state stabilization that is denied to a polarity-mismatched reaction.

Although the combination of steps 1 and 3 in [Scheme 1](#) achieves the same result as step 2 in [Scheme 2](#) (see Figure 3), the polarity-matched steps in Scheme 1 can be fast enough that in combination they are more rapid, sometimes much more rapid, than the single, polarity-mismatched step in Scheme 2. When this occurs, the added thiol is said to catalyze the entire reaction by polarity-reversal catalysis.<sup>10</sup> The next three sections describe reactions that either are made possible by or have improved yields due to polarity-reversal catalysis.

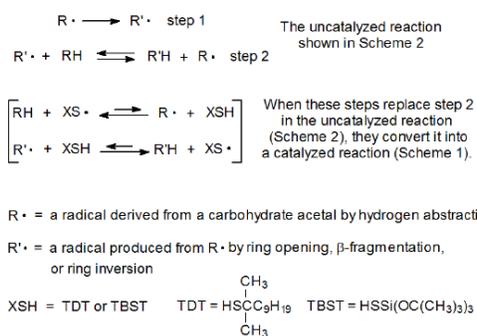


Figure 3. Catalyzed and uncatalyzed hydrogen-atom transfer

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