

# Prompt Dissociations of Small Combustion Radicals

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## Abstract

In combustion chemistry, it is commonly assumed that species formation and decay steps are distinct, with many thermalizing collisions occurring prior to decomposition. However, recent theoretical studies [1,2] have indicated that a weakly-bound radical such as HCO dissociates so rapidly at high temperatures that the dissociation process interferes with the collisional internal energy relaxation process as it occurs within vibrational-rotational relaxation time scales. Under such conditions ( $T > 1000$  K), “prompt” dissociation of HCO to  $H + CO$  occurs as part of the vibrational-rotational relaxation process. Simulations [1,2] using detailed kinetics models revealed that laminar flame speeds for hydrocarbon and oxygenated fuels are influenced when incorporating HCO “prompt” dissociation. Hydrocarbon and oxygenated radicals [3-7] with larger density of states and low bond-dissociation energies can also be expected to exhibit non-equilibrium effects leading to “prompt” dissociations at high temperatures. In this present work, we have computed non-equilibrium factors and corresponding direct dissociation probabilities for small hydrocarbon and oxygenated radicals ( $C_2H_3$ ,  $C_2H_5$ ,  $C_3H_5$ ,  $n-C_3H_7$ ,  $i-C_3H_7$ ,  $CH_3O$ ,  $CH_2OH$ ,  $CH_3CO$ ,  $CH_3CHOH$ , and  $CH_3CH_2O$ ). These direct dissociation probabilities were then incorporated into detailed kinetics models relevant to simulating combustion. The role of “prompt” dissociations of these and other radicals will be discussed in the context of the combustion simulations performed in this work.

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