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secondary isotope effect

A kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the rate-controlling step or in a pre-equilibrium step of a specified reaction, and is therefore not a primary isotope effect. One speaks of α, β, (etc.) secondary isotope effects, where α, β, (etc.) denote the position of isotopic substitution relative to the reaction centre. The corresponding isotope effect on the equilibrium constant of such a reaction is called a 'secondary equilibrium isotope effect'. Secondary isotope effects have been discussed in terms of the conventional electronic effects of physical organic chemistry, e.g. induction, hyperconjugation, hybridization, etc., since these properties are determined by the electron distribution, that depends on vibrationally averaged bond lengths and angles which vary slightly with isotopic substitution. While this usage is legitimate, the term 'electronic isotope effect' should be avoided, because of the misleading implication that such an effect is electronic rather than vibrational in origin.
See also: steric isotope effect

Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1131