

CARBOCATION NMR ISOTOPE SHIFTS ANALOGOUS TO INVERSE γ -DEUTERIUM ISOTOPE EFFECTS

David A. Forsyth*, James S. Puckace, and Frances E. Shawcross

Department of Chemistry, Northeastern University
Boston, Massachusetts 02115

Abstract: Long-range NMR isotope shifts due to γ -deuteration in carbocations are upfield, in contrast to β -deuteration effects. Such behavior is analogous to kinetic and equilibrium isotope effects in carbocation-forming reactions.

Long-range intrinsic NMR isotope shifts in carbocations show behavior analogous to kinetic and equilibrium isotope effects in cation-forming reactions. For NMR isotope shifts at ^{19}F due to β -deuteration in *p*-fluorophenylcarbenium ions, similarities to β -deuterium kinetic and equilibrium isotope effects have previously been found in the angular dependence, additivity behavior, and dependence on electron demand.¹⁻³ We now wish to report that the analogy is maintained with respect to the effects of γ -deuteration. The analogy is remarkable because intrinsic NMR isotope shifts are associated with a particular structure and its set of force constants rather than with a change in force constants during a reaction, as in kinetic or equilibrium isotope effects. Also, intrinsic NMR isotope shifts arise from the effects of isotopic mass on the vibrationally averaged nuclear shieldings in a single structure, rather than from mass effects on the difference in vibrational energy content between two structures.

The Table summarizes isotope effects on the ^{19}F chemical shift of *p*-fluorophenylcarbenium ions, 1-4, due to deuterium labeling in β and γ positions, where the benzylic cation center is defined as the α position. Each isotope shift was measured from a solution containing unequal amounts of the labeled and unlabeled cation, so that the direction of the shift could be determined. The results in the Table are given in ppb per deuterium, but the measurements used cations fully labeled at the indicated positions. The cations were prepared from the appropriately labeled alcohols by ionization with $\text{FSO}_3\text{H}/\text{SbF}_5$ in SO_2ClF at -78°C . ^1H -Decoupled ^{19}F NMR spectra were measured at 56.2 MHz on a JEOL FX-60Q NMR spectrometer.

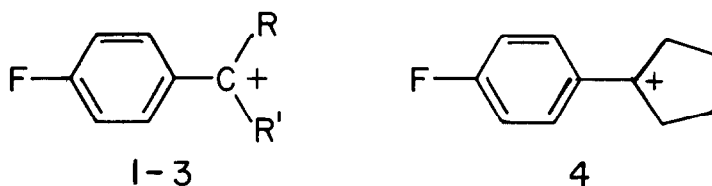


Table. ^{19}F NMR Isotope Shifts (ppb) per Deuterium in R' of Cations 1-4

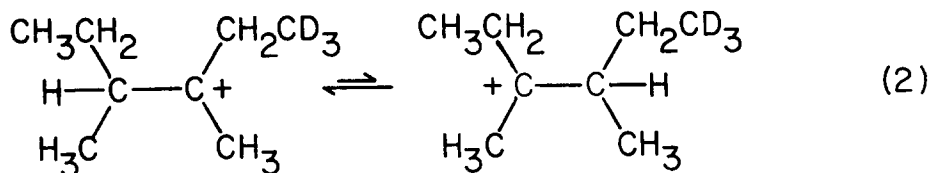
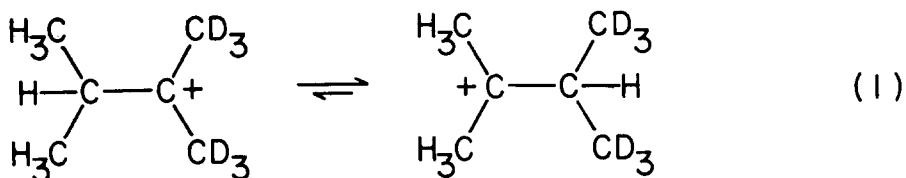
R	R'	$\beta\text{-D}$	$\gamma\text{-D}$
CH_3	CH_3CH_2	90	-20
CH_3CH_2	CH_3CH_2	36	-16
CH_3	$\text{CH}(\text{CH}_3)_2$	43	-14
	$-(\text{CH}_2)_4-$	150	-15

All of the isotope shifts due to β -deuteration are downfield, while γ -deuteration produces upfield isotope shifts. Downfield shifts have previously been interpreted as indicating that β C-D bonds behave as poorer electron donors in hyperconjugation than β C-H bonds,¹⁻⁴ based on the well-established relation between electron densities and ^{19}F chemical shifts in para substituted fluorobenzenes.⁵ Now, γ -deuteration apparently has the opposite effect of increasing the electron-donating character of an alkyl group.

The seeming alteration of electronic character of an alkyl group by isotopic substitution is not a violation of the Born-Oppenheimer approximation. NMR isotope shifts occur because the observed shielding of a nucleus is a vibrationally averaged property and average geometries differ between isotopomers. Bonds to deuterium have lower zero point vibrational energies and smaller vibrational amplitudes than bonds to hydrogen, and, within anharmonic energy surfaces for stretching motions, these mass-based differences result in average C-D bond lengths that are shorter than C-H bonds.⁶ Bond angles in isotopomers may also differ due to different averaging over bending motions. In this context, the manner in which γ -deuterium substitution could increase the electron-donating character of an alkyl group can best be understood by considering how the C-H bond vibrations are involved as an alkyl group interacts with a cation center.

The involvement of alkyl C-H bonds in cationic stabilization may be seen in isotope effects of energetic origin. Kinetic and equilibrium isotope effects are explicable on the basis of changes in relative zero-point vibrational energy levels for C-H and C-D bonds between two structures, the

reactant and the transition structure or product. Secondary kinetic isotope effects due to β -deuteration are typically normal ($k_H/k_D > 1$) in carbocation-forming reactions and are thought to occur primarily because hyperconjugative interactions of the β C-H(D) bonds with a developing vacant p orbital weaken the stretching and bending force constants of these bonds in the transition structure.⁷⁻¹¹ In an equilibrium, deuterium is found preferentially in the more tightly bound, nonhyperconjugating positions, as in eq (1).¹²



Few data are available for kinetic γ -deuterium effects, but the typical isotope effect is considered to be inverse ($k_H/k_D < 1$).^{9,10} Similarly, for the equilibrium shown in eq (2), deuterium prefers to be in the γ -position relative to the cation center rather than the more remote δ -position.¹³ Force constants are apparently strengthened for the γ C-H bonds of an alkyl chain which is interacting with a cation center.

Kinetic and equilibrium isotope effects thus indicate that alkyl interaction with a cation center typically weakens force constants for β C-H bonds and strengthens them for γ C-H bonds, relative to the bonding character in neutral precursors. The structure of the alkyl group in a particular carbocation represents a balance between the internal bonding requirements of the alkyl group and electron redistribution in stabilizing the cation center by hyperconjugative, inductive and field effects. However, to the extent that deuterium substitution perturbs the vibrationally averaged structure, the average electronic character will also be altered. In the simplest analysis, since a C-D bond is shorter than a C-H bond, we suggest that deuteration will enhance the electron-donating interactions that already lead to shortening of γ C-H bonds. However, substitution of shorter C-D bonds for C-H bonds will oppose the natural tendency of hyperconjugating β C-H bonds to become longer, so that β -deuteration will reduce the electron-donating character of an alkyl group.

The results also suggest a conformational dependence of isotope shifts for

both β and γ deuteration. The isotope shift due to β deuteration in 2 is only 40% as large as the isotope shift in 1. The γ C-D effect is also smaller in 2 than in 1, although the difference is not so dramatic. These differences are probably associated with a difference in planarity of the ethyl groups with respect to the benzylic framework in 1 and 2. The use of isotope shifts as a conformational probe has already been established,^{2,3,14} and will be discussed in detail in relation to these ions and others in a full paper.

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