

Theoretical Studies of Isotope Effects Pertinent to Solvolysis Mechanisms

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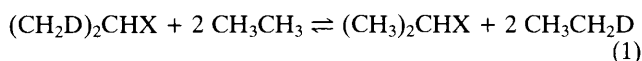
Secondary α -D and β -D₆ equilibrium isotope effects are calculated by *ab initio* MO methods for gas-phase heterolyses of a range of 2-propyl substrates; an anomalous trend in the β -D₆ effects with variation of the leaving group is accounted for by a model involving hyperconjugative and inductive contributions.

Secondary deuterium isotope effects constitute an important tool for mechanistic investigations of solvolytic reactions.^{1,2} It is commonly assumed for an S_N1 solvolysis that an α -D or β -D kinetic isotope effect (KIE) varies in magnitude between unity for a transition state resembling the reactant RX and a maximal value for a transition state resembling the product carbocation R⁺. An experimental KIE may therefore be interpreted as a measure of transition-state structure, provided that the limiting value is known. Doubt has been cast,³ however, upon the assumed maximal α -D KIEs for solvolyses of simple secondary alkyl halides and arenosulphonates.¹ Since the maximal KIE is (in the absence of tunnelling) approximately equal to the equilibrium isotope effect (EIE) for $RX \rightleftharpoons R^+$, it would be desirable to know these values for solvent-unassisted, limiting S_N1 solvolyses of a range of secondary alkyl substrates with different leaving groups X. These EIEs would be difficult to measure experimentally but are ideally suited to calculation by *ab initio* SCF MO methods.[†] We report calculated α -D and β -D₆ EIEs for formation of the 2-propyl cation from a range of substrates (CH₃)₂CHX, where X = H, F, OH, OH₂⁺, and N₂⁺. These theoretical results shed new light on the origin of secondary α -D and β -D isotope effects.

The calculated α -D EIEs for X = H and F (Table 1) are similar to those obtained from empirical force-field calculations,³ and that for X = OH₂⁺ accords with values of 1.29 and 1.35 determined experimentally for acid-catalysed dehydrations of benzhydrol and 4,4'-dichlorobenzhydrol.⁸ There is a linear correlation ($r = 0.996$) between the α -D EIE and the bending force constant F_{XCH} , given by $K_H/K_{\alpha-D} = 0.86 F_{XCH} + 0.67$; the larger the value of F_{XCH} in the reactant, the larger the magnitude of the normal EIE, in accord with expectation.⁹

On the basis of the commonly accepted hyperconjugative origin of β -D isotope effects in solvolytic reactions,^{2,10} it was expected that, as X became a better leaving group, the magnitude of the normal β -D₆ EIE for RX heterolysis would decrease as the substrate acquired more carbocationic character. Along the series X = H, OH, F, and OH₂⁺, the increasing degree of planarity at C_α and the decreasing length of the C_αC_β bond (Table 1) both suggested an increase in carbocationic character for the 2-propyl group in (CH₃)₂CHX. However, the calculated β -D₆ EIE actually increases along this series. The fact that the average β -CH bond length decreases along the same series (Table 1) provides a hint that the origin of these EIEs is not entirely hyperconjugative.

The calculated free-energy change ΔG for the equilibrium (1) was evaluated as a function of θ , the dihedral angle



[†] Harmonic force constants were calculated for the optimised geometry of each molecule at the RHF/4-31G level of theory,⁴ using the CADPAC program,⁵ and were scaled⁶ by 0.82; isotope effects were obtained, following normal-co-ordinate analysis, by evaluation of free-energy contributions within the ideal-gas, rigid-rotor, harmonic-oscillator approximation.^{6,7}

DC_βC_αX, using the geometrically distinct pairs of H_β atoms in the optimised 2-propyl structures. These data may be modelled by the relation (2) which expresses the conforma-

$$-\Delta G(\theta, X) = 2RT (H_X \cos^2\theta + I_X) \quad (2)$$

tional dependence of the isotopic fractionation factor for H vs. D in a pair of equivalent β -CH bonds of a particular 2-propyl substrate relative to ethane. The coefficient H_X determines the importance of the angularly dependent hyperconjugative contribution, and the constant I_X reflects the contribution of a conformationally independent (inductive?) effect. As the CX bond becomes more polar the value of H_X increases but I_X becomes more negative (Table 2). The β -D₆ EIE for heterolysis of (CH₃)₂CHX' is equal to the ratio of equilibrium constants for equation (1) with X' = X and X' = null (the 2-propyl cation), and within this model may be estimated as the product of three β -D₂ EIEs, one for each pair of β -CH bonds, calculated using equation (2). As X becomes a better leaving group, the hyperconjugative factor in these β -D₆ EIEs decreases whereas the inductive factor becomes less inverse and approaches unity (Table 2). The product of these factors reproduces the (apparently) anomalous trend in the β -D₆ EIEs and yields values in agreement with the directly calculated isotope effects given in Table 1.

The magnitudes of both the hyperconjugative and inductive contributions depend upon the requirement for stabilisation of the incipient carbocationic centre at C_α: this requirement may be diminished by the presence of a poorer leaving group or of a more nucleophilic solvent.¹¹ A value of ca. 0.985 is often assumed for an inductive β -D KIE in solution^{1,2} but a larger effect of 0.944 has been found for solvolysis of a cholestanyl brosylate,¹² comparable with values of ca. 0.93 and ca. 0.96 calculated as $(K_H/K_{\beta-D_6})^{1/6}$, from Table 2, for X = F and OH₂⁺. These inductive isotope effects are calculated within the harmonic approximation and do not require an explanation based on anharmonicity of CH stretching vibrations.² The cos² θ angular dependence of β -D EIEs and

Table 1. 4-31G Calculated equilibrium isotope effects for (CH₃)₂CHX \rightleftharpoons (CH₃)₂CH⁺ at 25 °C and some structural features for (CH₃)₂CHX.

X	$K_H/K_{\alpha-D}$	F_{XCH}^a	$K_H/K_{\beta-D_6}$	Planarity at C _α ^b	Bond length (Å)	
					C _α C _β	<C _β H _β > ^c
H	1.121	0.54	1.544	0.09	1.530	1.0840
OH	1.338	0.78	1.570	0.12	1.523	1.0832
F	1.317	0.76	1.678	0.26	1.512	1.0818
OH ₂ ⁺	1.315	0.73	1.776	0.56	1.502	1.0815
N ₂ ⁺	1.032	0.41	1.119	0.99	1.456	1.0854
() ^d	1		1.00	1.00	1.451	1.0869

^a Valence force constant for XCH bending co-ordinate, units of md Å rad⁻². ^b Fractional change in the sum of the angles C_βC_αH, C_βC_αH and C_βC_αC_β between 3 × 109.47° and 360°. ^c Average of six values. ^d 2-Propyl cation.

Table 2. A conformationally dependent model for β -D equilibrium isotope effects on heterolysis of $(\text{CH}_3)_2\text{CHX}$ at 25 °C, based on equations (1) and (2).

X	H_X	I_X	$K_H/H_{\beta\text{-D}_6}$		
			Hyperconjugative	Inductive	Product
H	0.003	0.008	2.68	0.58	1.54
OH	0.001	0.007	2.70	0.58	1.57
F	0.023	-0.015	2.53	0.66	1.67
OH_2^+	0.069	-0.023	2.22	0.80	1.78
N_2^+	0.318	-0.085	1.12	1.00	1.12
() ^a	0.362	-0.084	1	1	1

^a 2-Propyl cation.

analysis into hyperconjugative and inductive contributions were previously discussed by Hehre and coworkers¹³ in regard only to approximate changes in zero-point vibrational energy for classical-ethyl-cation formation from ethane, using idealised geometries and considering only CH stretching force constants. Our analysis is based upon complete isotope effects calculated using full harmonic force fields at optimised geometries of a range of 2-propyl substrates with different leaving groups.

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