β-Secondary Deuterium Isotope Effects as a Measure of Charge Localization in Carbonium Ion Reactions: the Existence of a Major Inconsistency in Interpretation

By Stuart E. Scheppele

(*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma* 74074)

Summary In contrast to published interpretations, the solvolytic β-deuterium isotope effects for secondary and tertiary norborn-2-yl derivatives are qualitatively inconsistent with anchimerically assisted solvolysis for *exo*-secondary substrates.

THE small β-deuterium isotope effects for *exo*-norborn-2-yl derivatives (I) have been adduced as evidence supporting anchimerically assisted solvolysis of (I), *i.e.*, charge dispersal on to C-1 and C-6.[1] The normal β-effects for *endo*-norborn-2-yl[1] and *exo*- and *endo*-2-methyl[2] and -2-phenyl-norbornyl[3] derivatives have been attributed to unassisted solvolysis with normal transition state charge localization at C-2.[1-3] Consequently, the delocalization of the incipient positive charge by a 2-methyl and 2-phenyl group in the transition state of these tertiary derivatives must be at least as great as that by the 3-centred (C-1, C-2, C-6) molecular orbital in the transition state of (I).

It is reported here that the β-effects for (I) are not satisfactorily explained by non-classical charge delocalization and, hence, the effects appear to be inconsistent with anchimerically assisted solvolysis of (I).

(I) *exo* -X·   (III) *exo* -X   (V) *exo* -X
(II) *endo* -X   (IV) *endo* -X   (VI) *endo* -X
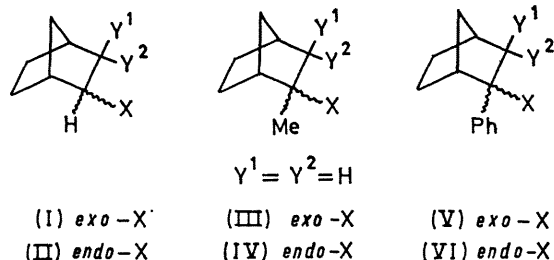
Hyperconjugation[4] and relief of non-bonded interactions[5] have been suggested to be the origin of the force constant change associated with the β-hydrogens in passing from the reactant to transition state.[6] Although steric isotope effects have been observed,[7] the available data[4,8] indicate that hyperconjugation, when possible, is the dominant factor.[7f,8e] For a S_N1 reaction, the β-effect is a function of the magnitude of the positive charge at C_α[8e] and the dihedral angle, ϕ, between the β-hydrogen and the incipient *p*-orbital on C_α,[8b,c] *e.g.*, for tertiary chlorides the β-effect per D varies from 1·31—0·99 as ϕ is varied from 180(0)—90°.[8c] For large (small) values of ϕ the magnitude of k_H/k_D for arenesulphonate solvolysis appears to be greater.[8c,9]

Dideuteriation at C-3 in *exo*-(I)(X = Br or $O \cdot SO_2Ph$, OBs) results in a significantly reduced isotope effect (see Table). The data for (Ib) and (Ic) show that the β-effect in (Ia) results principally from the *exo*-3-D. The β-effect for $[3,3-^2H_2]$-(II), (IIa), is normal; similar isotope effects are observed for (IIb) (*exo*-3-D) and (IIc) (*endo*-3-D), respectively.

For a transition state involving participation leading to a non-classical carbonium ion, hyperconjugation should be

β-Deuterium isotope effects in the solvolysis of norborn-2-yl derivatives

	X	Y¹	Y²	(k_H/k_D)[a,b]	Ref.
(Ia)	Br	D	D	1·04[c], 1·02[d]	1a
(Ia)	OBs	D	D	1·014;[e] 1·06,[f] 1·11[f,g]; 1·03[h]	1b,c
(Ib)	OBs	D	H	1·11[f]; 1·07[h]	1c
(Ic)	OBs	H	D	1·01;[f] 1·01[h]	1c
(IIa)	Br	D	D	1·16;[i] 1·30[g,i]	1a
(IIb)	OBs	D	H	1·19[f]	1c
(IIc)	OBs	H	D	1·12[f]	1c
(IIIa)	OPNB	D	D	1·334[g,j]	2
(IVa)	OPNB	D	D	1·306[g,j]	2
(Va)	OPNB	D	D	1·18[g,k]	3
(VIa)	OPNB	D	D	1·15[g,k]	3

[a] Rate ratio with respect to the non-deuteriated compound, *e.g.* (I)/(Ia): [b] isotope effect per D unless otherwise specified; [c] calcd. from polarimetric rate constants; [d] calcd. from titrimetric rate constants; [e] solvent HOAc; [f] solvent 80% aq. EtOH; [g] k_H/k_D for 2 atoms of β-D; [h] solvent KOAc–HOAc; [i] solvent aq. EtOH; [j] solvent aq. acetone; [k] solvent aq. dioxan.

more important for exo-3-H (ϕ ca. 180°) than for endo-3-H (ϕ ca. 60°).[1c] For a transition state leading to a classical ion both exo- and endo- 3-H are equally disposed towards the incipient p-orbital on C_α (ϕ ca. 30°).[1c] The diminished isotope effect for (Ib) over its expected value of ca. 1·18[9] to 1·31,[8c] the negligible effect for (Ic) together with the data for (Ia) have been interpreted as supporting anchimeric assistance to ionization.[1] Charge delocalization and the unfavourable stereochemistry negates hyperconjugation for the endo-3-H.[1c]

The data for (IIa), (IIb) (exo-3-D), and (IIc) (endo-3-D) are consistent with solvolysis without participation.[1] In agreement with this conclusion are the similar β-effects for solvolysis of cis-2-D (ca. 1·15) and trans-2-D (ca. 1·19) cyclopentyl toluene-p-sulphonates.[9] Further support for this conclusion has been deduced from the β-effects for (III), (IV), (V), and (VI) (X = O·CO· C_6H_4·NO_2-p,OPNB) which indicate for these tertiary substrates solvolysis without participation and charge development at C-2 in the transition state of similar magnitude to that for (II).[2,3] The 2-phenylnorbornyl cation (VII) is indicated by n.m.r. analysis to be classical and possess charge dispersal and stabilization similar to that for the 1-phenylcyclopentyl and 1-phenylcyclohexyl cations.[10] The reduced β-effects for (Va) and (VIa) are consistent with decreased hyperconjugation resulting from charge dispersal on to the aromatic ring.[8e]

However, this interpretation of the data in the Table contains a major inconsistency. Replacement of the C-2 hydrogen in the non-classical transition state for (I) by a 2-methyl or 2-phenyl group provides sufficient stabilization either significantly to reduce or to negate bridging. Consequently, to compensate for the loss in bridging in the solvolytic transition state for these tertiary derivatives, the dispersal of positive charge from C-2 on to either the methyl group via induction and hyperconjugation or phenyl via conjugation must be at least as great as charge delocalization on to C-1 and C-6 in the transition state for (I). Assuming anchimerically assisted ionization for (I), β-effects in the solvolysis of the tertiary substrates would have been predicted a priori to be similar to, if not smaller than, those of (Ia; X = Br or OBs). This prediction is in direct contrast to the experimental results and the previous conclusions

drawn from these results. Charge density at C-2 in the transition states of (III) and (IV) is indicated as normal[8,9] and similar to that for (II) (anchimerically unassisted solvolysis). Furthermore, the β-effects for (III)—(VI) compared to (II) suggest that a 2-methyl or 2-phenyl substituent has a negligible or small effect on the reactant-like:product-like character of the transition state leading to a classical norbornyl cation. Possible effects of steric hindrance to hyperconjugative release,[1c] steric crowding of the C-3 hydrogens,[1c] or possible variations in the dihedral angles in the transition states for the present compounds could afford an adequate explanation of these inconsistencies. Unfortunately such effects cannot be quantified at present. However, the isotope effects and the n.m.r. data for (VII) are qualitatively consistent with "normal" solvolytic transition states for (II)—(VI). Alternatively, the β-effect for (I) does not appear to be consistent, at least qualitatively, with either the non-classical or classical theories.

An explanation for the β-effect for (I) and the other compounds in the Table must also account for the differences in deuterium isotope effects at C-2[9,11] and C-6[12] between (I) and (II) and at C-6 between (I) and 1,2-dimethyl-exo-norborn-2-yl p-nitrobenzoate,[13] data which have been interpreted as substantiating anchimerically assisted solvolysis for (I).[1-3,11-13]

The available data indicate a difference in the force constant(s) change associated with the hydrogens at C-2, C-3, and C-6 accompanying conversion of (I) and (II) into their transition states. A precise calculation of these force field changes which would deduce the bonding in the transition states for (I) and (II) and, hence, resolve the problem of the solvolysis mechanism of (I)[14] is at present impossible. The uncertainty in the qualitative interpretation of the β-effects in the Table may possibly bear on the interpretation of the deuterium isotope effects at other positions. Consequently, additional isotope effect data are required to provide a detailed explanation for these results.

[1] (a) J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, J. Amer. Chem. Soc., 1967, 89, 6938; (b) J. M. Jerkunica, S. Borcic, and D. E. Sunko, Chem. Comm., 1967, 1302; (c) B. L. Murr and J. A. Conkling, J. Amer. Chem. Soc., 1970, 92, 3464.

[2] J. M. Jerkunica, S. Borcic, and D. E. Sunko, Chem. Comm., 1968, 1488.

[3] J. P. Schaefer, J. P. Foster, M. J. Dagani, and L. M. Honig, J. Amer. Chem. Soc., 1968, 90, 4497.

[4] For leading references see (a) V. J. Shiner, jun., J. Amer. Chem. Soc., 1953, 75, 2925; (b) E. S. Lewis and C. E. Boozer, ibid., 1952, 74, 6306; (c) E. A. Halevi, Progr. Phys. Org. Chem., 1963, 1, 109.

[5] (a) L. S. Bartell, J. Chem. Phys., 1960, 32, 827; Tetrahedron, 1962, 17, 177; J. Amer. Chem. Soc., 1961, 83, 3567.

[6] M. Wolfsberg and M. J. Stern, Pure and Appl. Chem., 1964, 8, 325.

[7] For leading references see (a) L. Melander and R. E. Carter, J. Amer. Chem. Soc., 1964, 86, 295; (b) K. Mislow, K.R. Graeve, A. J. Gordon, and G. H. Wahl, jun., ibid., p. 1733; (c) V. R. Raaen, T. K. Dunham, D. D. Thompson, and C. J. Collins, ibid., 1963, 85, 3497; (d) H. C. Brown and G. J. McDonald, ibid., 1966, 88, 2514; (e) H. C. Brown, M. E. Azzaro, J. G. Koelling, and G. J. McDonald, ibid., p. 2520; (f) G. J. Karabatsos, G. C. Sonnichsen, C. G. Papaioannou, S. E. Scheppele, and R. L. Shone, ibid., 1967, 89, 463; (g) E. D. Kaplan and E. R. Thorton, ibid., p. 6644.

[8] For leading references see (a) V. J. Shiner, jun., J. Amer. Chem. Soc., 1961, 83, 240; (b) V. J. Shiner, jun., B. L. Murr, and G Heineman, ibid., 1963, 85, 2413; (c) V. J. Shiner, jun., and J. S. Humphrey, jun., ibid., p. 2416; (d) V. J. Shiner, jun., and J. G Jewett, ibid., 1964, 86, 945; (e) V. J. Shiner, jun., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, ibid., 1968, 90, 418.

[9] (a) A. Streitwieser, jun., R. H. Jagow, R. C. Fahey, and S. Suzuki, J. Amer. Chem. Soc., 1958, 80, 2326; (b) J. O. Stoffer and J. D. Christen, ibid., 1970, 92, 3190.

[10] D. G. Farnum and G. Mehta, J. Amer. Chem. Soc., 1969, 91, 3256.

[11] (a) C. C. Lee and E. W. C. Wong, J. Amer. Chem. Soc., 1964, 86, 2752; (b) B. L. Murr and J. A. Conkling, ibid., 1970, 92, 3462; (c) C. C. Lee and E. W. C. Wong, Canad. J. Chem., 1965, 43, 2254.

[12] B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, J. Amer. Chem. Soc., 1967, 89, 1730; (b) J. M. Jerkunica, S. Borcic, and D. E. Sunko, ibid., p. 1732.

[13] H. L. Goering and K. Humski, J. Amer. Chem. Soc., 1969, 91, 4594.

[14] (a) S. Winstein and D. S. Trifan, J. Amer. Chem. Soc., 1949, 71, 2953; (b) H. C. Brown, Chem. in Britain, 1966, 2, 199.