

# A computational study on the sources of deuterium secondary kinetic isotope effects in carbocation-forming reactions

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**Abstract:** Calculations at the HF-DFT hybrid Becke3LYP level of theory have been undertaken on protonated 2-*exo*- and 2-*endo*-norbornanols as model substrates for 2-*exo*- and 2-*endo*-norbornyl brosylates to explore the source of the experimentally determined deuterium secondary kinetic isotope effects (KIEs). Calculations on protonated alcohols as models reproduce the “normal” behaviour of 2-*endo* substrate **5**. The observed *endo*  $\gamma$ -KIE in the 7-unsubstituted 2-*exo* system **4** is shown to arise from internal return, while those in the 7-chloro substituted 2-*exo* substrates **1** and **2** can be explained with competing 1,3 (6,2)-elimination.

**Key words:** deuterium secondary kinetic isotope effects, 2-norbornyl cation, Becke3LYP.

**Résumé :** Utilisant les formes protonées des 2-*exo*- et 2-*endo*-norbornanols comme modèles des brosylates des 2-*exo*- et 2-*endo*-norbornyles, on a effectué des calculs au niveau théorique hybride Becke3LYP HF-DFT afin d'explorer la source des effets isotopiques cinétiques (EIC) secondaires du deutérium observés expérimentalement. Les calculs sur les alcools protonés utilisés comme modèles permettent de reproduire le comportement « normal » du substrat 2-*endo* (**5**). On a démontré que l'EIC- $\gamma$  *endo* observé dans le système 2-*exo* non substitué en position 7 (**4**) découle d'un retour interne alors que l'on peut expliquer ceux observés avec les substrats 2-*exo* substitués par un chlore en position 7 (**1** et **2**) en invoquant une réaction d'élimination-1,3 (6,2) compétitive.

**Mots clés :** effets isotopiques cinétiques secondaires du deutérium, cation 2-norbornyle, Becke3LYP.

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Deuterium secondary kinetic isotope effects (KIEs) have been used for decades to gain information on reaction intermediates and transition states, which forms the basis of widely used structure–reactivity principles. Representative of these studies is the work of Werstiuk et al. on **1-OBs** and **2-OBs** (**1**) and **3** (**2**), which was undertaken to probe the degree of C<sup>6</sup>–C<sup>1</sup> participation in the cation-forming step of the solvolysis reactions in NaOAc-buffered 80:20 EtOH–H<sub>2</sub>O.

Earlier it was shown that *exo*-2-norbornyl brosylate-*exo*-6-*d* (**4-OBs6ex**) and *exo*-2-norbornyl brosylate-*endo*-6-*d* (**4-OBs6en**) exhibit unusually large  $\gamma$ -KIEs (**4-OBs6ex**: 9%, **4-OBs6en**: 11%), and the results were interpreted on the basis of a C<sup>6</sup>–C<sup>1</sup> bond assistance in the solvolyses ( $k_{\Delta}$ , X = H) (**3**) (Scheme 1). While *endo*-2-norbornyl brosylate-*exo*-6-*d* (**5-OBs6ex**) did not exhibit a  $\gamma$ -KIE, that of *endo*-2-norbornyl brosylate-*endo*-6-*d* (**5-OBs6en**) was slightly inverse



L = OBs, OH<sub>2</sub><sup>+</sup>

	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X	X'
<b>1-5ex6ex</b>	H	D	D	Cl	H
<b>2-5ex6ex</b>	H	D	D	H	Cl
<b>1-6en</b>	D	H	H	Cl	H
<b>2-6en</b>	D	H	H	H	Cl

R = H, D

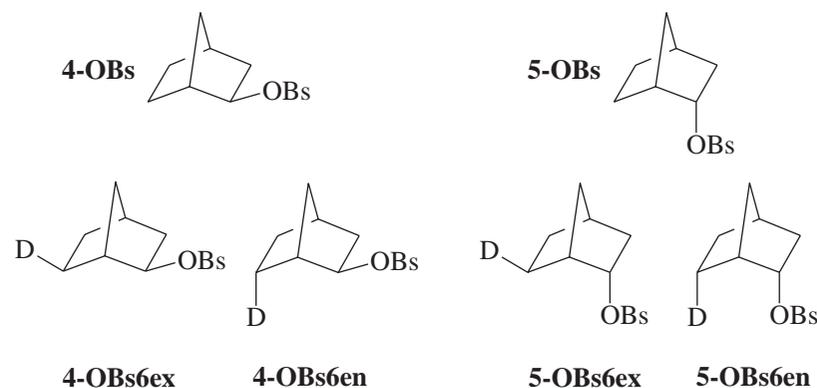
(3%). Similar results were obtained from acetolysis reactions (**4**). It was reasoned that a strong electron-withdrawing substituent at C<sup>1</sup> or C<sup>7</sup> should reduce the contribution of the  $k_{\Delta}$  process (**1**), as the build up of a partial positive charge on C<sup>1</sup> would become less favourable.

Unexpectedly,  $\gamma$ -KIEs in *anti*- and *syn*-7-chloro-*exo*-2-norbornyl brosylate-*exo,exo*-5,6-*d*<sub>2</sub> (**1-OBs5ex6ex**: 15%, **2-OBs5ex6ex**: 12%) and *anti*- and *syn*-7-chloro-*exo*-2-norbornyl brosylate-*endo*-6-*d* (**1-OBs6en**: 12%, **2-OBs6en**: 13%) were found to be larger than those found for the parent *exo* substrate **4-OBs**. This was interpreted with a combination of ef-

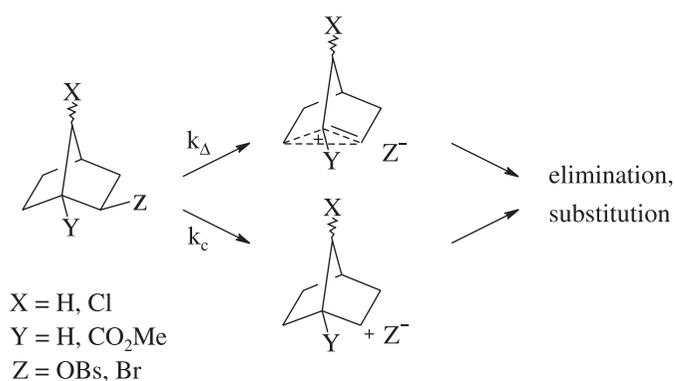
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Scheme 1.



fects instead of a simple C<sup>6</sup>—C<sup>1</sup> bond participation (considered were 1,3 elimination, *endo* hydrogen participation, 6,2-hydride shift, and solvent-assisted ionization), yet a final clarification was not achieved (1). Moreover, the unusually large  $\gamma$ -KIE found for bromoester **3** exhibited a solvent-polarity dependence (14% in 0.09 M NaOAc buffered 80:20 EtOH–H<sub>2</sub>O and 20% in 0.14 M NaOAc buffered 80:20 EtOH–H<sub>2</sub>O) (2). While the authors (1–4) drew conclusions from the experimental data (KIEs, products) and from analogous reactions, definitive statements could not be made at that time. Today, the full force of quantum chemical calculations can be brought to bear on problems of this type to gain fundamental information not directly accessible experimentally and, as a result, provide definitive solutions (see, for example, ref. 5). In this communication, we report the results of a computational study (using Gaussian 94 (6)) of deuterium secondary KIEs of systems **1**, **2**, **4**, and **5**.

As the brosylate systems are prohibitively large, it was necessary to find a reasonable level of theory as well as suitable model systems for substrates and solvolysis transition states. The problems in describing the 2-norbornyl cation are well known and have been confirmed by a computational study by Schleyer and co-workers (7): the classical 2-norbornyl cation (**7**) is a transition state in the rearrangement from the 2-norpinyl cation (**6**) to the — what so far has been referred to as “nonclassical” — 2-norbornyl cation (**8**); this

result was achieved at the MP2(full)/6-31G(d) level of theory that was termed “adequate” because **7** was found not to be a stationary point at the HF/6-31G(d) level. In a more recent paper it is stated that a similar structure for **7** could be calculated using Becke3LYP/6-31G(d) (8). Our excellent experiences with the HF-DFT hybrid theory Becke3LYP (9) for different systems and chemical problems (10) led us to employ the computationally quite inexpensive Becke3LYP/6-31G(d,p) level of theory,<sup>2</sup> the inclusion of polarization functions on the hydrogen atoms being essential for the intended study of deuterium KIEs. We found that the 2-norbornyl cation can be described adequately at this level of theory: transition state **7** exhibits the one desired imaginary frequency (–266.6 cm<sup>–1</sup>) and an IRC calculation links **7** to **6** and **8**. According to Becke3LYP/6-31G(d,p), **7** lies 13.17 kcal mol<sup>–1</sup> above **8**,<sup>3</sup> which is in excellent agreement with the 13.64 kcal mol<sup>–1</sup> found with MP4(sdq,fc)/6-31G(d,p)/MP2(full)/6-31G(d) (13.1 kcal mol<sup>–1</sup> with Becke 3LYP/6-311+G(d) (8)) reported by Schleyer and co-workers (7a). We therefore carried out geometry optimizations as well as frequency calculations using Becke3LYP/6-31G(d,p).

We assumed<sup>4</sup> that an optimized protonated alcohol is a good model for a reactant with the neutral leaving group water forcing the positive charge onto the hydrocarbon fragment in the transition state for dissociation. To test this approach, we calculated secondary  $\alpha$ - and  $\beta$ -KIEs for a “normal” system, cyclopentyl brosylate (**9-OBs**). The KIE is computed as the ratio of the rate constant for the undeuterated (light) species over that for the deuterated (heavy) one. Secondary KIEs were determined with the program MacIEcalc<sup>5</sup> from masses, moments of inertia, and frequencies of light and heavy reactants as well as light and heavy transition states (TS) with the temperature set at 298.15 K if not stated otherwise. As scaling factors for Becke3LYP calculations are very close to 1.0, frequencies were not scaled (11); secondary KIEs do not require correction for a tunneling effect. A transition state for the dissociation of the protonated cyclopentanol could not be located, but computed KIEs using models for the TS, in which the C—O distance in the protonated alcohol is fixed at either 210 or 250 pm, were compared to experimental ones as determined by Stoffer and Christen (12) (KIEs in Table 1). With the 210

<sup>2</sup>See refs. 5a and b; in these papers, Houk and co-workers conclude that Becke3LYP calculations provide good predictions of KIEs.

<sup>3</sup>Zero-point energy uncorrected total energies are –273.060433 hartrees for **7** and –273.081420 for **8**.

<sup>4</sup>This work was started before ref. 8 was available.

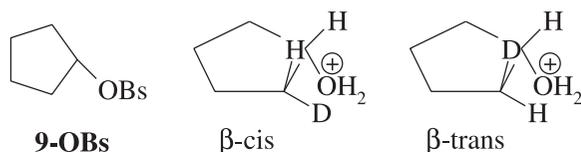
<sup>5</sup>K. Korzekwa, J. Urbauer, D. Kiick, and J. Jones (changes by W.H. Saunders). University of Rochester, Rochester, N.Y.

**Table 1.** Experimental and calculated  $\alpha$ -,  $\beta$ -, and  $\gamma$ -KIEs for **1**, **2**, **4**, **5**, and **9**. Calculations employ the transition state (TS, with C—O distances as given in Fig. 1) and 180, 210, and 310 pm models of the protonated alcohols.

	Deuterium position	Expt. <sup>a</sup>	Model			
			TS	180 pm	210 pm	310 pm
<b>1-5ex6ex</b>	$\gamma,\delta$	$1.150 \pm 0.013^b$	1.166		1.082	
<b>1-6en</b>	$\gamma$	$1.120 \pm 0.005^b$	1.064		1.003	
<b>2-5ex6ex</b>	$\gamma,\delta$	$1.119 \pm 0.011^b$	1.131 <sup>c</sup>		1.045	
<b>2-6en</b>	$\gamma$	$1.125 \pm 0.007^b$	1.028 <sup>c</sup>		1.001	
<b>4-6ex</b>	$\gamma$	$1.09 \pm 0.01^d$	1.127	1.015	1.051	1.130
<b>4-6en</b>	$\gamma$	$1.11 \pm 0.01^d$	1.054	0.999	0.998	1.045
<b>4-3en3ex</b>	$\beta,\beta$	$1.10^{e,f}$	1.066 <sup>f</sup>	1.037 <sup>f</sup>	1.113 <sup>f</sup>	1.106 <sup>f</sup>
<b>4-5ex6ex</b>	$\gamma,\delta$	1.09 <sup>g</sup>	1.126	1.017	1.053	1.132
<b>5-6ex</b>	$\gamma$	$1.00 \pm 0.02^{d,h}$	1.015 <sup>h</sup>		0.997 <sup>h</sup>	
<b>5-6en</b>	$\gamma$	$0.97 \pm 0.01^{d,h}$	0.949 <sup>h</sup>		0.969 <sup>h</sup>	
<b>5-2ex</b>	$\alpha$	1.20 <sup>h,i</sup>	1.203 <sup>h</sup>		1.144 <sup>h</sup>	
<b>5-3en3ex</b>	$\beta,\beta$	1.26 <sup>i,k</sup>	1.285 <sup>k</sup>		1.141 <sup>k</sup>	
<b>5-5ex6ex</b>	$\gamma,\delta$	1.00 <sup>f,k</sup>	1.015 <sup>k</sup>		0.993 <sup>k</sup>	
<b>9</b>	$\alpha$	1.187 <sup>l</sup>			1.148 (1.238) <sup>m</sup>	
<b>9</b>	$\beta$ -cis	1.153 <sup>l</sup>			1.053 <sup>n</sup> (1.161) <sup>m,o</sup>	
<b>9</b>	$\beta$ -trans	1.180 <sup>l</sup>			1.141 <sup>p</sup> (1.206) <sup>m,q</sup>	
<b>9</b>	$\beta^r$	1.888 <sup>l</sup>			1.443 (1.959) <sup>m</sup>	

<sup>a</sup>For the brosylates.<sup>b</sup>Reference 1.<sup>c</sup>For the 290 pm model.<sup>d</sup>Reference 3.<sup>e</sup>Reference 13.<sup>f</sup>At 317.45 K.<sup>g</sup>Reference 14.<sup>h</sup>At 323.15 K.<sup>i</sup>Reference 15.<sup>j</sup>Reference 16.<sup>k</sup>At 338.15 K.<sup>l</sup>Reference 12.<sup>m</sup>For the 250 pm model.<sup>n</sup>From 1.093 and 1.015 for nonequivalent positions 2 and 5.<sup>o</sup>From 1.039 and 1.297 for nonequivalent positions 2 and 5.<sup>p</sup>From 1.073 and 1.214 for nonequivalent positions 2 and 5.<sup>q</sup>From 1.059 and 1.374 for nonequivalent positions 2 and 5.<sup>r</sup>2,2,5,5-Tetrasubstitution.

pm model, all calculated KIEs for **9** are smaller than the experimental values, while all are slightly too large at 250 pm.



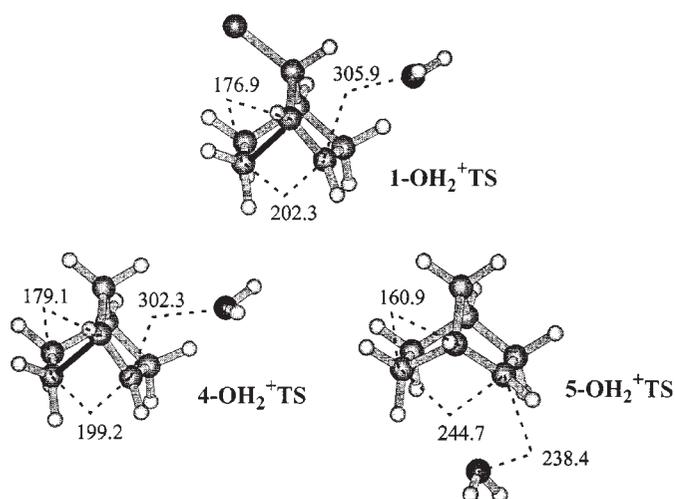
These results suggest that the C—O distance in the TS lies between 210 and 250 pm, providing support for our choice of model.

The located transition-state geometries<sup>6</sup> for **4-OH<sub>2</sub><sup>+</sup>** and **5-OH<sub>2</sub><sup>+</sup>** resemble those reported (8), and **1-OH<sub>2</sub><sup>+</sup>** is similar to **4-OH<sub>2</sub><sup>+</sup>** (so far we have not been successful in locating the transition state for the *syn*-7-chloro-*exo*-2-nor-

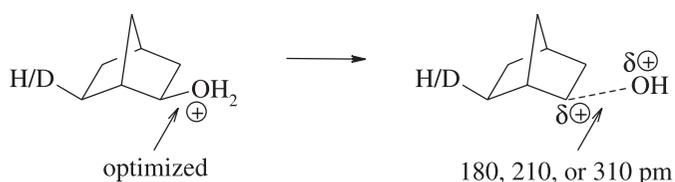
bornyl brosylate (**2**), but a model with the C—O distance at 290 pm was taken as an approximation to **2-OH<sub>2</sub><sup>+</sup>**TS). The hydrocarbon fragment in each transition state is distinctly unsymmetrical as can be seen from the C<sup>6</sup>—C<sup>1</sup> and C<sup>6</sup>—C<sup>2</sup> distances given in Fig. 1, and even though the *exo* transition states **1-OH<sub>2</sub><sup>+</sup>**TS and **4-OH<sub>2</sub><sup>+</sup>**TS are closer to being symmetrical than the *endo* transition state **5-OH<sub>2</sub><sup>+</sup>**TS, it is important to note that *all three hydrocarbon cation moieties are classical*, contrary to the interpretation of Schleyer and co-workers (8); a situation that is emphasized in Fig. 1 by means of the highlighted bond for **1-OH<sub>2</sub><sup>+</sup>**TS and **4-OH<sub>2</sub><sup>+</sup>**TS. The topology of the charge density of the 2-norbornyl cation that has been moved from C<sub>s</sub> symmetry as determined in an atoms in molecules (17) study shows a (3,−1) or bond critical point only between C<sup>6</sup> and C<sup>1</sup>, not between C<sup>6</sup> and C<sup>2</sup>, and confirms the classical character of every struc-

<sup>6</sup>Zero-point energy uncorrected total energies are −809.111584 (**1-OH<sub>2</sub><sup>+</sup>**), −809.102719 (**1-OH<sub>2</sub><sup>+</sup>**TS), −809.129369 (**2-OH<sub>2</sub><sup>+</sup>**), −349.527681 (**4-OH<sub>2</sub><sup>+</sup>**), −349.518000 (**4-OH<sub>2</sub><sup>+</sup>**TS), −349.524206 (**5**), and −349.512550 hartrees (**5-OH<sub>2</sub><sup>+</sup>**TS).

**Fig. 1.** Transitions states (TS) for the loss of water from protonated alcohols **1-OH<sub>2</sub><sup>+</sup>**, **4-OH<sub>2</sub><sup>+</sup>**, and **5-OH<sub>2</sub><sup>+</sup>** with C—O and C—O distances in pm. See text for the highlighted bond.



**Scheme 2.**

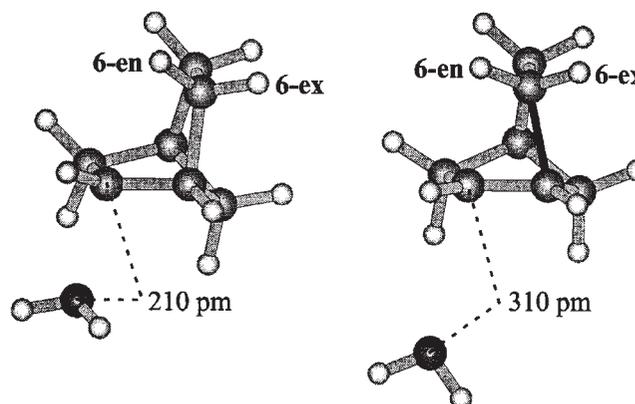


ture but the  $C_S$  symmetrical one — which is a  $\pi$ -complex, as was suggested earlier by Dewar et al. (18)! A communication reporting these results has been submitted (19).

To gain some further insight into the source of the KIEs, the transition states were also modelled by fixing the C—O bond in the protonated alcohol at an appropriate value (we chose 210 pm) and optimizing the resulting system. These pseudo-transition states, just as the true gas-phase transition states, show one imaginary frequency that has the expected dispositions. Additionally, we performed calculations for 180 and 310 pm C—O distances in **4-OH<sub>2</sub><sup>+</sup>**. The absolute value of the imaginary frequency is largest for the 210 pm model of **4-OH<sub>2</sub><sup>+</sup>** ( $-120.1\text{ cm}^{-1}$ ); it is considerably smaller for the 310 pm model ( $-45.7\text{ cm}^{-1}$ ) and for **4-OH<sub>2</sub><sup>+</sup>TS** ( $-51.3\text{ cm}^{-1}$ ) and nonexistent in the 180 pm model (the lowest frequency is  $91.0\text{ cm}^{-1}$ ), Scheme 2.

Table 1 gives the computational results and comparisons to experiment for deuterated derivatives of **1**, **2**, **4**, and **5**. Five different KIEs of *endo*-2-norbornyl brosylate (**5-OBs**) can be determined with excellent accuracy in the gas phase when **5-OH<sub>2</sub><sup>+</sup>TS** is used (entry TS in Table 1). Both normal and inverse KIEs are modelled correctly with only little overestimation. Accordingly, there are no surprises with the 210 pm model of **5**. While the calculated  $\alpha$ -effect in **5-OH<sub>2</sub><sup>+</sup>2ex** and the  $\beta$ -effect in the doubly deuterated **5-**

**Fig. 2.** Gas-phase structures of **4-OH<sub>2</sub><sup>+</sup>** with the C—O distance at 210 and 310 pm. See text for the highlighted bond.



**OH<sub>2</sub><sup>+</sup>3en3ex** are slightly too small, as expected due to the 210 pm distance, which is shorter than the one in **5-OH<sub>2</sub><sup>+</sup>TS** (Fig. 1), the experimentally observed absence of a  $\gamma$ -effect in **5-OBs6ex** and **5-OBs5ex6ex** is confirmed computationally, as is the modest inverse  $\gamma$ -effect in **5-OBs6en**. The situation is more complicated for *exo*-2-norbornyl brosylate (**4-OBs**). With **4-OH<sub>2</sub><sup>+</sup>TS**, none of the four computed KIEs seems to show a particularly good agreement with experiment, the  $\gamma$ -effect in **4-OBs6ex** and **4-OBs5ex6ex** being overestimated and the  $\beta$ -effect in **4-OBs3en3ex** underestimated. The calculated KIE in **4-OH<sub>2</sub><sup>+</sup>6en** seems to present the worst case. Using **4-OH<sub>2</sub><sup>+</sup>TS** it is much too small, and calculations on the 210 pm model even predict the absence of any  $\gamma$ -KIE, whereas experimentally the largest KIE was found for the brosylate (11%) (1). We repeated gas-phase calculations for **4-OH<sub>2</sub><sup>+</sup>** with C—O distances of 180 and 310 pm. As expected, a C—O distance of 180 pm is too close to the optimized C—O bond length of 163.7 pm and therefore a poor model for a transition state: the  $\gamma$ -effect in **4-OH<sub>2</sub><sup>+</sup>6ex** is very small, there is no effect for **4-OH<sub>2</sub><sup>+</sup>6en**. Going to a C—O distance of 310 pm gives rise to a significant  $\gamma$ -KIE in **4-OH<sub>2</sub><sup>+</sup>6en**. These three TS models allow a step-by-step approach to the geometry change in the hydrocarbon moiety upon ionization and its effects. Figure 2 shows that the 2-norbornyl cation, which is definitely unsymmetrical at 210 pm (with distances C<sup>6</sup>—C<sup>1</sup> 161.8 pm and C<sup>6</sup>—C<sup>2</sup> 230.3 pm), is closer to being symmetrical (C<sup>6</sup>—C<sup>1</sup> 175.2 pm and C<sup>6</sup>—C<sup>2</sup> 203.7 pm) at a water distance of 310 pm where the distinction between *endo* and *exo* deuterium on C<sup>6</sup> is fading with beginning internal return (the structures given in Fig. 2, with one highlighted bond for the 310 pm model, represent the molecular graphs as determined in an atoms in molecules study (19)). This view finds support in the average KIE of **4-OH<sub>2</sub><sup>+</sup>6ex** and **4-OH<sub>2</sub><sup>+</sup>6en**, which equals 1.09 and so represents the experimental value (observed KIEs for **4-OBs6ex** and **4-OBs6en** are identical within experimental error), and also in the early acetolysis study (4), which gives initial KIEs that are in accord with those computed, i.e., a significantly smaller value for **4-OBs6en**:  $1.149 \pm 0.016$  for **4-OBs6ex** and  $1.097 \pm 0.011$  for **4-OBs6en**. For *exo* substrates *anti*-7-chloro **1-OBs** and *syn*-7-chloro **2-OBs**, we calculate *exo* KIEs that agree well with the observed ones whereas the *endo* KIEs, similar to **4-OH<sub>2</sub><sup>+</sup>6en**, are too small. Yet unlike the case of **4-OBs**, major solvolysis products for

**1-OBS6en** (13%) and **2-OBS6en** (20%) are the respective chloronortricyclenes formed through a 1,3 (6,2)-elimination with the *endo* deuterium being lost preferentially (close to 80% deuterium loss) (1), and it has been shown in a steady-state treatment of a modified Winstein ion-pair scheme (2) that (and how) the isotope effects for elimination from ion pairs can contribute to  $k_H/k_D$ .

In conclusion, deuterium secondary kinetic isotope effects are computed accurately at the Becke3LYP/6-31G(d,p) level of theory when solvolysis transition states are employed. Sources for observed KIEs can be explored and resolved with Becke3LYP calculations.

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