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Preliminary Communication **$\beta$ -Deuterium Isotope Effect in Solvolysis of 1,2-Dimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate**

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Secondary  $\beta$ -deuterium isotope effects have been shown to be remarkably constant with change of solvent<sup>1</sup>. The ratio,  $k_H/k_{D_3}$ , was 1.22 in solvolysis of 1-phenylethyl chloride in ethanol-water mixtures ranging from 50 vol % to 80 vol % of ethanol. It was proposed that the transition state is very nearly the same in all the solvents studied. The yields of styrene (as an elimination product) were between 1 and 3 percent.

It was also found<sup>2</sup> that the  $\beta$ -isotope effect on solvolysis of *t*-butyl- $d_9$  chloride was 2.62 in 97 wt % trifluoroethanol-water and 2.49 in 70 wt % trifluoroethanol. In 97% trifluoroethanol 30% of olefin was obtained but only 17% in 70% trifluoroethanol. One possible interpretation given for the discrepancy in the effects is based on ion pair return competing with rate-determining elimination.

The  $\beta$ -hydrogen isotope effect and product composition in the solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (I) in the dioxane-water mixtures, ranging from 50 vol % to 70 vol % of dioxane, has been measured and the results are presented in the Table.

Compound I was synthesized as described previously<sup>3</sup>, while 1,2-dimethyl-*exo*-2-norbornyl-3,3- $d_2$  *p*-nitrobenzoate (II) was obtained from 1-methyl-2-norbornanone-3,3- $d_2$ <sup>3</sup>. The deuterated ketone was prepared by the hydrogen-deuterium exchange of the ketone in heavy water and deuterated trifluoroacetic acid and contained 1.78 atoms of deuterium per molecule (according to mass spectra).

The titrimetric rates were obtained employing the automatic potentiometric titration method maintaining a constant pH of 6.8. The rate constants were calculated from the standard integrated first-order rate law using the non-linear least square program\*. No trend was observed in the constants between 20% to 80% of reaction completion.

The product study was conducted in the usual way using the ampoule technique in the presence of a slight excess (20% to 30%) of 2,6-lutidine (to neutralize the acid produced by solvolysis)<sup>4</sup>. The products were found to be stable under the reaction conditions.

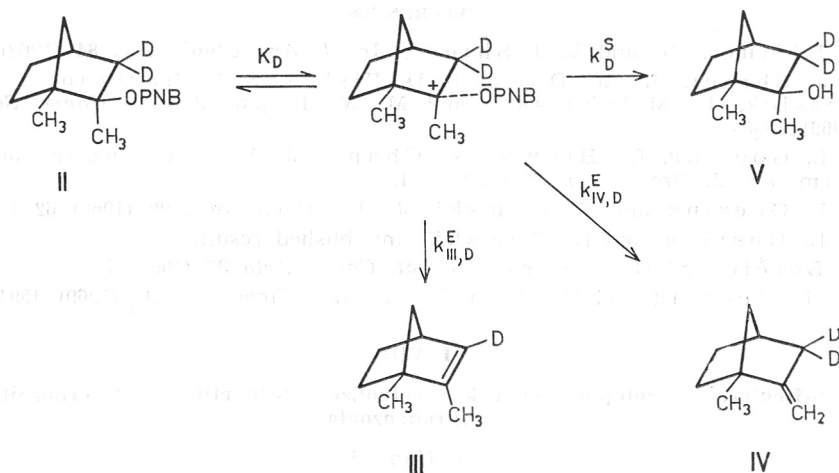
From the Table it is evident that the measured isotope effect,  $k_H/k_D$ , is directly related to the amount of elimination product formed. This indicates that the elimination is rate-determining and in competition with the substitution and internal return, as shown in the following scheme.

\* The author thanks Dr. L. Klasinc for this computer program.

TABLE  
 First-Order Rate Constants, Product Compositions and Isotope Effects for Solvolysis of Undeuterated (I) and 3,3,  
 Dideuterated 1,2-Dimethyl-exo-2-norbornyl p-Nitrobenzoate (II) in Dioxane-Water Mixtures at 69.30° C

Dioxane Vol %	Comp. <sup>a</sup>	10 <sup>3</sup> k, min <sup>-1</sup> , b	k <sub>H</sub> /k <sub>D</sub>	Product in % <sup>c</sup>					k <sub>III, H</sub> <sup>E</sup> /k <sub>III, D</sub> <sup>E</sup>	k <sub>H</sub> /k <sub>D</sub>
				III	IV	V	VI	VII		
50	I	24.52 ± 0.12	1.278 ± 0.010	18.7	17.6	63.7			1.92	1.20
	II	19.18 ± 0.10		10.8	16.1	73.1				
55	I	13.19 ± 0.07	1.294 ± 0.011	13.5	16.7	69.6			1.46	1.23
	II	10.20 ± 0.07		9.7	16.5	73.7				
60	I	6.754 ± 0.042	1.317 ± 0.012	19.7	18.7	61.6			1.27	1.23
	II	5.129 ± 0.036		16.2	23.2	60.6				
65	I	3.376 ± 0.091	1.360 ± 0.049	21.2	20.5	58.4			1.10	1.26
	II	2.483 ± 0.060		19.7	26.8	53.4				
70	I	1.583 ± 0.042	1.351 ± 0.079	35.5	30.6	33.9			1.98	1.18
	II	1.172 ± 0.061		21.7	28.1	50.4				
						average:			1.54	1.22

<sup>a</sup>Initial concentration less than 0.006 M for each measurement. <sup>b</sup>Each entry represents 6-8 measurements; uncertainties are standard errors. <sup>c</sup>Compositions based on weighed capillary gipc peak areas; each entry represents the average of four injections from two independent samples.



This scheme is an oversimplification because it is known that more than one carbonium ion is involved in the solvolysis of I<sup>4</sup>. Namely, solvolysing optically active I, in either 90 vol % aqueous acetone or anhydrous methanol the elimination product IV retained ~ 60% of the original optical activity while the substitution product V had only ~ 10% of optical activity<sup>4</sup>. This indicates that substitution probably occurs from a solvent separated ion pair whereas the elimination ensues from an intimate ion pair. It was also shown that the solvolysis is accompanied by internal return but no evidence for an external return was found<sup>5</sup>. The absence of external return justifies an irreversible process for  $k^S$  in spite of the fact that more than one ion is involved in the product forming step. The observed rate constants are then given by the following expressions

$$k_H = K_H (k_{III,H}^E + k_{IV,H}^E + k_H^S)$$

$$k_D = K_D (k_{III,D}^E + k_{IV,H}^E + k_D^S)$$

The assumption was made that  $k_H^S = k_D^S$ . This is reasonable since the ionization process is known to be a major source of the secondary isotope effects<sup>6</sup>. From the product study it is possible to calculate the primary isotope effect for the formation of the elimination product, III. The value  $k_{III,H}^E / k_{III,D}^E$  is not very precise because a small error in measuring III results in a large change in isotopic rate ratio.

The resultant secondary isotope effect,  $K_H/K_D$ , is fairly constant with change of solvent composition. The value, 1.22, is in agreement with other measured β-secondary hydrogen isotope effects. Such a result is also in agreement with other evidence obtained in this system, supporting the view that the ionization of 1,2-dimethyl -exo-2-norbornyl derivatives is not strongly assisted<sup>4,7</sup>.

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## IZVOD

 **$\beta$ -Deuterijski izotopni efekat kod solvolize 1,2-dimetil-egzo-2-norbornil *p*-nitrobenzoata**

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Izmjereni su  $\beta$ -deuterijski izotopni efekti kod solvolize 1,2-dimetil-egzo-2-norbornil-3,3- $d_2$  *p*-nitrobenzoata u smjesama dioksan-voda. Također je određen sastav smjese produkata ovih solvoliza. Iz dobivenih rezultata zaključeno je da ukupna vrijednost izotopnog efekta uključuje i primarni izotopni efekat za nastajanje eliminacionog produkta. To je jedino moguće ako je proces eliminacije onaj stupanj koji određuje brzinu reakcije.

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ZAGREB

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