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ISOTOPE EFFECTS. II. FURTHER COMMENTS ON THE CONTRIBUTION ON NONBONDED INTERACTIONS TO SECONDARY DEUTERIUM ISOTOPE EFFECTS.

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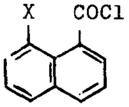
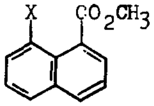
In a recent communication (1) we concluded that reasonable estimates of secondary deuterium isotope effects caused by nonbonded interactions may be obtained by using Bartell's procedure (2). Particularly disturbing was the discrepancy between the experimental isotope effect, $\Delta\Delta G^{\ddagger} = \Delta G_H^{\ddagger} - \Delta G_D^{\ddagger} = -16.6 \pm 8.3$ cal/mole and $k_H/k_D = 1.029$ at 25°, obtained in the limiting solvolysis of I, and the calculated ΔΔE of about -100 to -300



I_a X = CH_3
I_b X = CD_3

cal/mole.

Nonbonded interactions should affect mainly $\Delta\Delta H^{\ddagger}$ of the isotope effect. To draw more reliable conclusions, therefore, on the contribution on nonbonded interactions to secondary deuterium isotope effects, the calculated effect should be compared to that part of the experimental effect that is due to enthalpy rather than free energy differences. We have, therefore, measured the isotope effects of the limiting solvolysis of I and the basic hydrolysis of II as a function of temperature and wish to comment on their relevance to the



II_a X = CH_3
II_b X = CD_3

problem.

In Table I we have summarized the pertinent data of the solvolyses (3) and I and II.

The striking difference between the 13-17% isotope effect observed in the solvolysis of I at low temperatures and the 2.9% observed (4) at 25° cogently illustrates how the isotope effect at 25° could have led to the wrong conclusion regarding the contribution of nonbonded interactions to secondary isotope effects. The -308 cal/mole value of $\Delta\Delta H^{\ddagger}$ agrees with the -200 ± 100 cal/mole $\Delta\Delta E$ calculated (1) from nonbonded interactions. Also in agreement with the $\Delta\Delta E$ value of about +200 to +400 cal/mole calculated (5) for the basic hydrolysis of II are the experimentally measured isotope effects (Table 1).

Table 1

Cpd.	Temp., °C (±0.005°)	$k \times 10^4$ sec^{-1}	$\Delta H^{\ddagger}$ cal/mole	$\Delta S^{\ddagger}$ e.u.	k_{CH_3}/k_{CD_3}	$\Delta\Delta G^{\ddagger}$ [b] cal/mole	$\Delta\Delta H^{\ddagger}$ [b,c] cal/mole
I_a	-34.003	1.0065± 0.0022	16,955± 89	-5.5± 0.4			
I_b	"	0.8618± 0.0056		-4.5± 0.1	1.168± 0.009	-74±4	-308± 102
I_a	-26.613	2.980± 0.042					
I_b	"	2.645± 0.053	17,262± 13		1.127± 0.018	-59±8	
I_a	-20.453	7.21± 0.17					
I_b	"	6.386± 0.012			1.130± 0.027	-61±11	
II_a+II_b	61.5±0.5				0.84± 0.02	+116±16	
II_a+II_b	79.5±0.5				0.89± 0.02	+82±15	

[a] Compound I was solvolyzed in 75.23/24.77 (W/W) acetone-water. The hydrolysis of II was carried out in 1N sodium hydroxide in ethanol. [b] $\Delta\Delta G^{\ddagger} = \Delta G_H^{\ddagger} - \Delta G_D^{\ddagger}$ and $\Delta\Delta H^{\ddagger} = \Delta H_H^{\ddagger} - \Delta H_D^{\ddagger}$. [c] Calculated from a plot of $\ln(k_H/k_D)$ vs. 1/T.

Conceivably, therefore, some secondary deuterium isotope effects might be strongly temperature dependent (6). If so, and regardless of the source of such dependence, conclusions drawn from secondary deuterium isotope effects measured at a single temperature should be treated with due caution (7).

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References

(1) G. J. Karabatsos, G. C. Sonnichsen, C. G. Papaioannou, S. E. Scheppele, and R. L. Shone, J. Am. Chem. Soc., 89, 463 (1967).

(2) L. S. Bartell, ibid., 83, 3567 (1961).

(3) The solvolyses of the acid chlorides were studied by conductance. The data have been treated statistically by a least squares computer program. The reported standard deviations are σ values of the usual 68% confidence limits. As pointed out (1) the basic hydrolysis of II is too slow to determine individual rate constants. The isotope effects were determined by hydrolysis of almost equimolar mixtures of II_a and II_b in excess sodium hydroxide in ethanol and calculation of the moles of labeled and unlabeled acids produced after a certain reaction time . The calculation was carried out by measuring the total amount of acids obtained and determining their molar ratio by mass spectral analysis. Each k_H/k_D is the average of four determinations. We thank Mr. Seymour Meyerson of American Oil Company, Whiting, Indiana, for the mass spectral analyses.

(4) The room temperature studies were carried out in 95% (W/W) acetone-water. It should be pointed out that the isotope effect extrapolated to 25° by using the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values is about 2%.

(5) G. C. Sonnichsen, Ph. D. Thesis, Michigan State University, 1967.

(6) See also the unusual results presented by E. A. Halevi and Z. Margolin, Proc. Chem. Soc., 174 (1964).

(7) We wish to emphasize that the present results do not invalidate the conclusion (1) that in ordinary systems where hyperconjugation is possible the calculated nonbonded effect accounts for a small part of the experimental.