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DISSECTION OF ISOTOPE EFFECTS. IV. DISSECTED DEUTERIUM EFFECTS IN THE SOLVOLYSIS OF 2-OCTYL-3,3-$\underline{d}_2$ BROSYLATE IN 65% AQUEOUS ETHANOL AND THE QUESTION OF THE TEMPERATURE DEPENDENCE OF $\underline{\beta}$-DEUTERIUM EFFECTS

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We have proposed[1,2] that the usual study of isotope and other effects on overall reaction rates be supplemented by the investigation of what we have referred to as "dissected effects". These are effects on the partial rate constants for the formation of the individual reaction products $\underline{k}_i$, defined by equation (1) where $\underline{k}$ is the usual pseudo first order solvolytic reaction rate constant for the overall reaction, and $\underline{f}_i$ is the mole fraction of each $\underline{i}$th product. Application of this approach to isotope effects has introduced the "dissected isotope effects" for the pathways leading to the individual products, $(\underline{k}_i)_H/(\underline{k}_i)_D$ or DIE_i, defined by equation (2).

$$\underline{k}_i = \underline{f}_i\underline{k} \quad (1), \quad DIE_i = (\underline{k}_i)_H/(\underline{k}_i)_D = \underline{k}_H(\underline{f}_i)_H/\underline{k}_D(\underline{f}_i)_D \quad (2)$$

In our initial application of this approach to $\underline{\beta}$-deuterium effects in the solvolysis of 2-octyl brosylate in 65% aqueous ethanol,[2] we also interpreted the so obtained DIE's by treating them as kinetic effects, on the basis of the assumption that rate and product determining steps should be treated as being the same.[1-3a] As we suggested,[2] the use of such dissected effects in different systems and reaction conditions should contribute to their interpretation and to a test of the above assumption. This is done in the present communication by extending the study of the title system conducted initially at 54°[2] to its study at 73°. Comparison of the results at the two temperatures should contribute in this respect by giving at the same time information on the temperature dependence of $\underline{\beta}$-deuterium effects. The latter is known to be inconsistent and puzzling without a satisfactory answer, even though various interpretations have been discussed.[4-6] $\underline{\beta}$-Isotope effects in the solvolysis of alkyl sulfonates and halides have been found to increase, decrease, or remain unchanged with increasing temperature.[4-6] We anticipate[1,2] that this problem may prove to be due, at least partly, to inadequate understanding of $\underline{\beta}$-deuterium effect data.

Following these considerations, products (Table I) and rates (Table II) were determined in the solvolysis of 2-octyl brosylate (I) and I-3,3-$\underline{d}_2$ in 65% (Wt/Wt) aqueous ethanol at 54° and 73°. Our earlier determination of products at 54°[2] was repeated in the present study under conditions of still higher accuracy and identical to those in the experiments at 73°. Table II lists the overall reaction kinetic isotope effects $\underline{k}_H/\underline{k}_D$ and the DIE's at the two temperatures, and gives some of the resulting activation parameters. The present DIE values at 54° are very similar to those we obtained earlier.[2] This attests to their dependability and accuracy, as also do the very small standard errors of the present product data which are of the order of e.g. only ±0.05% for the 2-alcohol and ether products, or only ±0.5% for products (e.g. 3-octanol) formed to the extent of just 0.3% (Table I). These precisions were achieved as a result of a demanding volume of experimental work, improvements in techniques, and attention to details. High precision is necessary for detecting any small differences in the DIE's between the two temperatures, particularly since DIE's are products of the two ratios $\underline{k}_H/\underline{k}_D$ and $(\underline{f}_i)_H/(\underline{f}_i)_D$, a fact which tightens still further the already

TABLE I. Products in the Solvolysis of (I) and I-3,3-$\underline{d}_2$ in 65% (Wt/Wt) Aq.Ethanol at 54° and 73°

Product[a]	Yield in mole%, ($\underline{f}_i$ x 100)[b]			
	I (54°)	I-3,3-$\underline{d}_2$ (54°)	I (73°)	I-3,3-$\underline{d}_2$ (73°)
2-Octanol	49.898 ± 0.036	54.847 ± 0.052	47.913 ± 0.032	53.106 ± 0.042
2-Octyl ethyl ether	29.003 ± 0.021	31.827 ± 0.049	26.903 ± 0.026	30.030 ± 0.039
trans-2-Octene	11.836 ± 0.022	6.958 ± 0.023	13.613 ± 0.020	8.418 ± 0.022
cis-2-Octene	7.222 ± 0.014	4.201 ± 0.016	8.711 ± 0.015	5.331 ± 0.014
1-Octene	1.624_1 ± 0.0050	1.823_3 ± 0.0054	2.298_0 ± 0.0065	2.629 ± 0.010
3-Octanol	0.296_4 ± 0.0025	0.247_9 ± 0.0036	0.402_7 ± 0.0020	0.353_7 ± 0.0040
3-Octyl ethyl ether	0.120_5 ± 0.0017	0.095_9 ± 0.0023	0.159_8 ± 0.0017	0.132_7 ± 0.0025

[a] Products found to be stable to the reaction and GC conditions. [b] Yields are given in relative mole% (absolute recovery is 100% within experimental error). Each value represents the average of the yields obtained in over forty and twenty GC product determinations for I and I-3,3-$\underline{d}_2$ respectively. Uncertainties are standard errors for a 95% confidence interval, *i.e.* (standard error) x 1.96.

TABLE II. Isotope Effects in the Solvolysis of I-3,3-$\underline{d}_2$ in 65% (Wt/Wt) Aq.Ethanol at 54° and 73°

Product	$(\underline{k}_i)_H/(\underline{k}_i)_D$ [a,b]		$\Delta\Delta F_i^{\ddagger}$ (25°)[b,c] cal/mole	$\Delta\Delta E_i^{\ddagger}$ [b,c] cal/mole	$(\underline{A}_i)_H/(\underline{A}_i)_D$ [b,c]
	54°	73°			
Overall reaction	1.331_7 ± 0.0054[d]	1.333_4 ± 0.0045[d]	-168 ± 83[e]	+15 ± 48[f]	1.36 ± 0.13
2-Octanol	1.211_6 ± 0.0049	1.203_0 ± 0.0041	-121 ± 84	-84 ± 63	1.06 ± 0.10
2-Octyl ethyl ether	1.213_6 ± 0.0050	1.194_5 ± 0.0042	-131 ± 85	-187 ± 64	0.91 ± 0.09
trans-2-Octene	2.266 ± 0.010	2.156_3 ± 0.0080	-536 ± 92	-585 ± 69	0.92 ± 0.09
cis-2-Octene	2.289 ± 0.010	2.178_7 ± 0.0082	-542 ± 93	-584 ± 70	0.93 ± 0.10
1-Octene	1.186_2 ± 0.0054	1.165_3 ± 0.0048	-120 ± 97	-210 ± 73	0.86 ± 0.09
3-Octanol	1.592 ± 0.015	1.519 ± 0.011	-326 ±186	-565 ±140	0.67 ± 0.14
3-Octyl ethyl ether	1.674 ± 0.024	1.606 ± 0.018	-349 ±294	-492 ±221	0.79 ± 0.26

[a] Obtained in terms of eq. (2) from the $\underline{f}_i$'s (Table I) and $\underline{k}$'s (see below) of I and I-3,3-$\underline{d}_2$ respectively. [b] Uncertainties are standard errors. [c] Isotope effects on the "dissected" (based on, and calculated from the $\underline{k}_i$'s): free energies of activation, $\Delta\Delta F_i^{\ddagger}=(\Delta F_i^{\ddagger})_H-(\Delta F_i^{\ddagger})_D$; energies of activation, $\Delta\Delta E_i^{\ddagger}=(\Delta E_i^{\ddagger})_H-(\Delta E_i^{\ddagger})_D$; Arrhenius pre-exponential factors, $(\underline{A}_i)_H/(\underline{A}_i)_D$. [d] $\underline{k}_H/\underline{k}_D$ ratio, at 54° (2) and at 73°. The latter is obtained from the following rate constants, $\underline{k}$ x 10^2 min^{-1}, for the solvolysis at 73° of I and I-3,3-$\underline{d}_2$ respectively: 27.468 ± 0.062 and 20.600 ± 0.053 (uncertainties are standard errors). These values are the average of the rate constants obtained from 30 and 20 experiments for I and I-3,3-$\underline{d}_2$ respectively carried out by the pH-stat technique and numbering a total of about 85 readings for each experiment followed from 20 to 85% completion. [e] $\Delta\Delta\underline{F}^{\ddagger}$. [f] $\Delta\Delta\underline{E}^{\ddagger}$.

stringent requirements for accuracy in the usual determination of just $\underline{k}_H/\underline{k}_D$'s.

The overall reaction isotope effect $\underline{k}_H/\underline{k}_D$ is at 73° the same, if not slightly higher than at 54°, *i.e.* 1.333 *vs* 1.332 respectively; namely it is essentially temperature independent. The $\Delta\Delta\underline{E}^{\ddagger}$ value is near zero (+15 cal/mole), whereas $\Delta\Delta\underline{F}^{\ddagger}$ (-168 cal/mole) is much larger, and all of the isotope effect appears in the Arrhenius pre-exponential term which gives $\underline{A}_H/\underline{A}_D$ = 1.36, *i.e.* a ratio substantially larger than unity. These features are all analogous to those observed in the solvolyses of isopropyl derivatives in water,[4,6] where for isopropyl-$\underline{d}_6$ bromide, $\underline{k}_H/\underline{k}_D$ is 1.317 at 40° and 1.324 at 70°, $\Delta\Delta\underline{E}^{\ddagger}$ is +35 and $\Delta\Delta\underline{F}^{\ddagger}$ -179 cal/mole, and $\underline{A}_H/\underline{A}_D$ is 1.39. This behavior, which has been labelled "abnormal", has added to the complexity of the temperature dependence of β-deuterium effects. In fact, the solvolyses of these derivatives have been labelled the most abnormal ones.[4]

Let us now look at the DIE's. Their values at each temperature differ substantially, as was also observed at 54°,[2] and are respectively fairly similar at the two temperatures. Thus, the discussion and interpretation of the DIE's at 54° in our earlier publication[2] is applicable to the present results also. Additionally, this similarity in the results strengthens the validity of both sets of data. What is most significant however, and also the object of this study, is the exact comparison of the respective DIE's at the two temperatures. Such a comparison reveals that these DIE's, unlike the k_H/k_D ratio, differ between these temperatures, namely are temperature dependent. Very significantly, these isotope effects are all generally lower at the higher temperature. The isotope effects on the "dissected" Arrhenius term (A_i) and energy of activation ($\Delta F_i^{\ddagger}$ and $\Delta E_i^{\ddagger}$), namely on the A terms and energies of activation based on k_i's, also exhibit "normal" behavior. Thus, within experimental error, the $\Delta\Delta F_i^{\ddagger}$ values can be considered to be fairly similar to the $\Delta\Delta E_i^{\ddagger}$ ones, particularly for the major products, while the pre-exponential effects $(A_i)_H/(A_i)_D$ are generally slightly less than unity, although this is only nearly so for the 2-octanol forming path which gives an effect of 1.06. The above features, which are associated with "normal" behavior,[4] indicate that the DIE's in this solvolysis exhibit, within experimental error, a normal temperature dependence unlike the abnormal one shown by the k_H/k_D effect.

The present findings and our interpretation of DIE's suggest the following reasonable explanation for the lack of a dependence on temperature of our overall reaction isotope effect k_H/k_D.

Equation (2) can be written in the form of eq (3). Application of the latter to each ith of the n reaction products and summation of the resulting equations lead to eq (4). According to

$$(k_H/k_D)(f_i)_H = [(k_i)_H/(k_i)_D](f_i)_D \quad (3), \qquad k_H/k_D = \sum_{i=1}^{i=n}[(k_i)_H/(k_i)_D](f_i)_D \quad (4)$$

equation (4), which follows from the definition of DIE's (eq 2), the isotope effect k_H/k_D is equal to the sum of the DIE's of the individual products multiplied each by the mole fraction of the respective product of the deuterated derivative (I-3,3-d_2). If, additionally, our treatment of DIE's as kinetic effects[2] is accepted, then equation (4) would also suggest that the observed kinetic isotope effect k_H/k_D does not represent a single, or single reaction, isotope effect but is instead a composite effect made up and determined by different isotope effects of different products and in proportion to the relative yields of these products. In this case and for the system under study, the increase in the yields of the 2-octenes in going from 54° to 73°, even though of the order of only a few percent units, when coupled with the fact that the DIE values of these olefins are much higher than those of the other products, should contribute to an increase in the k_H/k_D effect. This increase, which is associated solely with the change in the product yields, happens to be approximately equal to a decrease in this overall isotope effect due to the temperature effect itself on the DIE's, thus resulting in the lack of a net change in k_H/k_D. This could be seen numerically also, if our DIE and $(f_i)_D$ values were introduced in eq (4). The resulting equations[7] for the 54° and 73° data, which lead to calculated k_H/k_D values of 1.332 and 1.333 respectively (equal to the experimental ones, as they have to be), illustrate numerically also that even though the isotope effect values introduced (DIE's) are all lower at 73° than at 54°, the so calculated overall reaction isotope effect k_H/k_D is not lower at 73°.

The present interpretation of the temperature dependence of β-isotope effects in our system, when generalized, suggests, tentatively since an assumption is involved, that observed β-k_H/k_D effects could decrease, increase, or remain unchanged with increasing temperature, and could do so even, and at best, if the "true" isotope effects had a single, and "normal", dependence on temperature. The actual behavior should depend, according to this interpretation, on a delicate balance between the "true" temperature effect on one hand, and on the difference between the DIE's of the different products and the effect of temperature on the relative yields of these products on the other hand.

The present findings are particularly significant in two ways. Firstly, they suggest a "reasonable" picture for the temperature dependence of β-deuterium effects, k_H/k_D's and DIE's, and offer an explanation for the inconsistent temperature dependence shown by β-k_H/k_D effects. They also point to a way for solving this problem and suggest that DIE's could contribute significantly in this respect. Additionally, these findings are in line with a position that β-deuterium effects in the present system, and possibly in the solvolysis of other alkyl sulfonates also could have basically a normal temperature dependence. Secondly, the above success of DIE's offers indirect evidence if favor of their interpretation (as kinetic effects) and of our position that the DIE's and not the k_H/k_D's contain the elements of significance,[1,2] at least in our system. This evidence is enhanced further by the fact that our earlier application of DIE's had also led to "reasonable" observations and interpretations.[2]

The implications of the present conclusions could be far reaching, as suggested earlier[1] concerning the significance of the approach of "dissection". Thus,isotope effects may have to be reinvestigated in terms of DIE's. If they are thus understood better, as we expect, they may prove to be still more useful a tool than believed, while some of the mechanistic deductions from k_H/k_D effects may have to be reappraised. Analogous implications are suggested also about the other usually studied effects on rates of solvolytic reactions. Additionally, evidence may thus be obtained concerning the mechanistic elements themselves which suggested[1-3a] this approach of "dissection". As indicated earlier,[1] these elements are associated with out theory of solvolyses[3b] and our objections[3c] to the ionization hypothesis and the resulting solvolytic mechanisms. We are certainly aware that the limited evidence presented in this and our earlier publications[1,2] is only a small step toward these implications. Nevertheless, these suggestions are useful guidelines for further investigations. Some of these are in progress in our laboratory.

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