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DISSECTION OF ISOTOPE EFFECTS. III[1] DISSECTED α-DEUTERIUM EFFECTS IN THE SOLVOLYSIS OF 2-OCTYL BROSYLATE IN 65% AQUEOUS ETHANOL

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Secondary kinetic deuterium effects provide one of the most subtle and powerful tools available for the investigation of reaction mechanisms.[2] However, these k_H/k_D effects, like most effects on the rates of solvolytic reactions, have usually been studied on overall reaction rates only.[2] We have criticized this approach and have attributed it mainly to the ionization hypothesis and the resulting treatment of solvolytic reactions to which we have long objected.[1,3] We have suggested[1] instead the study of "dissected effects", namely of effects on the partial rate constants for the formation of the individual reaction products, k_i, defined by equation (1), where k is the usual solvolytic reaction rate constant and f_i is the mole fraction of each ith product. Application of this approach to isotope effects has introduced the "dissected isotope effects", $(k_i)_H/(k_i)_D$, (DIE), defined by equation (2).[1b] A study of dissected β-isotope effects in the title solvolysis has been reported already.[1b] This communication report

$$k_i = f_i k \quad (1), \qquad (k_i)_H/(k_i)_D = (k_H/k_D)\left[(f_i)_H/(f_i)_D\right] \quad (2)$$

the determination of dissected α-isotope effects in the same system. These should be of additional interest in view of the particular and better understood relation believed to exist[2] between α-isotope effects and solvolytic mechanisms.

2-Octanol-2-d_1 was prepared by reduction of 2-octanone with lithium aluminum deuteride. 2-Octyl p-bromobenzenesulfonate (I) and I-2-d_1 were prepared respectively from 2-octanol and 2-octanol-2-d_1 by the usual procedure. Product and rate data determined for the solvolysis of these esters in 65% aqueous ethanol at 54° are given in the Table along with the resulting α-isotope effect k_H/k_D and the α-dissected isotope effects $(k_i)_H/(k_i)_D$.

The observed isotope effect is 1.121 at 54°. This value can be considered to be similar to the α-isotope effect reported for the solvolysis of 3-pentyl brosylate in 70 vol% aqueous ethanol which at 25° is 1.138[2] (α-isotope effects around 1.15 decrease[2] by about 0.01 units for every twenty degree increase in temperature). This similarity is in line with the accepted similarity in the mechanism of solvolysis of the straight chain saturated secondary alkyl sulfonates, and specifically 2-propyl, 2-butyl, 3-pentyl, and 2-octyl brosylates.[2] Thus, the interpretation given[2] to the α-isotope effect of 3-pentyl brosylate and to its relation to the mechanism of that solvolysis is supposed to apply to our system as well. This isotope effect, and α-isotope effects in the solvolysis of alkyl sulfonates in general have been discussed[2] in terms of their percent of the maximum effect of 1.22 observed[4] in the trifluoroacetolysis of isopropyl brosylate, and have been related to mechanism in terms of these percent values. Thus, different sections of such a scale have been associated[2] with different mechanisms within Winstein's ion pair scheme[5] with different steps being considered to be rate determining. Specifically, the α-isotope effect of 1.138 in the above ethanolysis of 3-pentyl brosylate has been associated by Shiner with a

TABLE I. Products, Rates, and Isotope Effects in the Solvolysis of 2-Octyl Brosylate (I) and I-2-$\underline{d}_1$ in 65% (Wt/Wt) Aqueous Ethanol at 54°

	Yield in mol% ($\underline{f}_i$ X 100) from:[b,c]		$\underline{k}$ X 10^{-2} min^{-1}[d,c]		$(\underline{k}_i)_H/(\underline{k}_i)_D$[e,c]
	I	I-2-$\underline{d}_1$	I	I-d-$\underline{d}_1$	
Overall reaction			4.425 ± 0.023	3.948 ± 0.021	1.121 ± 0.008[f]
2-Octanol	50.50 ± 0.10	51.09 ± 0.20			1.108 ± 0.010
2-Octyl eth.ether	29.04 ± 0.08	29.52 ± 0.10			1.103 ± 0.009
trans-2-octene	11.41 ± 0.05	10.80 ± 0.07			1.184 ± 0.013
cis-2-octene	7.02 ± 0.04	6.68 ± 0.05			1.178 ± 0.014
1-Octene	1.60 ± 0.01	1.50 ± 0.01			1.193 ± 0.017
3-Octanol	0.300 ± 0.003	0.287 ± 0.004			1.170 ± 0.022
3-Octyl eth.ether	0.135 ± 0.003	0.129 ± 0.003			1.173 ± 0.039

[a] Products found stable to the reaction and GC conditions. [b] Values are given in relative mol% (absolute recovery is 100% within experimental error). Each value represents the average of over twenty GC determinations (from eight runs) except for that for 3-octanol which is based on fewer measurements. [c] Uncertainties are standard errors for a 95% confidence interval (referring to precision). [d] These rate constants represent the average of those for twenty and fifteen experiments respectively for I (1b) and I-2-$\underline{d}_1$ carried out by the pH-stat technique and numbering a total of about seventy readings for each experiment which was followed from 15 to 85% completion. [e] Obtained from equation (2) from the overall reaction isotope effect $\underline{k}_H/\underline{k}_D$ (first entry in this column) and the mole fractions $(\underline{f}_i)_H$ and $(\underline{f}_i)_D$ given in this Table. [f] Overall reaction kinetic isotope effect $\underline{k}_H/\underline{k}_D$.

mechanism in which the formation of a tight ion pair is the rate-determining step.[2] This practice illustrates also the particular significance of such percent values in the case of $\underline{\alpha}$-isotope effects, and points to the need for their proper assignment and understanding.

Let us now apply our approach of dissection to the solvolysis under study. The rate and product data listed in the Table give in terms of equation (2) the dissected $\underline{\alpha}$-isotope effects shown in the same Table. Examination of these DIE's indicates that they differ not only from the overall reaction kinetic isotope effect $\underline{k}_H/\underline{k}_D$ but also between them. They vary in the range between 1.193 and 1.103 as compared to the value of 1.121 for the $\underline{k}_H/\underline{k}_D$ effect. The difference in the DIE's is greatest between the pathways leading respectively to elimination and to C-2 substitution products, with the DIE's for the elimination products being higher; e.g. the DIE for cis-2-octene is 1.178 as compared to 1.103 for the 2-octyl ethyl ether. Differences are also observed between the DIE's of the different olefins themselves, namely 1-octene and trans- and cis-octenes, as well as between the carbon-2 substitution products, 2-octanol and 2-octyl ethyl ether. However, these differences are too small and not outside the experimental errors to attach any significance to them at this point. The DIE's of the rearranged substitution products, 3-octanol and 3-octyl ethyl ether which must be formed by 1,2 hybride shift, are 1.170 and 1.173 respectively; however their relatively large uncertainties, ±0.02 and ±0.04 respectively, do not recommend their discussion at this time. Finally, in comparison to the overall reaction $\underline{k}_H/\underline{k}_D$ effect, the substitution product DIE's are lower whereas the elimination product ones are higher.

To proceed with an interpretation of these findings, we will make use of our assumption[1] that rate and product determining steps should be treated as being the same. Inversely, the discussion of DIE's with the use of this assumption and the very use itself of DIE's should contribute to an eventual interpretation of DIE's and to a test of this assumption, as suggested earlier.[1b] This assumption renders the DIE's in our system into kinetic effects and allows their direct comparison with the overall reaction kinetic isotope effect k_H/k_D. In this respect, equation (4) is useful. This equation results by rearrangement of equation (2) to equation (3) and application of the latter to each of the n reaction products followed by summation of the resulting equations.

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

Equation (4), which follows from the definition of DIE's, combined with our treatment of DIE's as kinetic effects suggest, tentatively since an assumption is involved, that *the observed k_H/k_D isotope effect*, which according to equation (4) is equal to the sum of the DIE's of the individual products multiplied each by the mole fraction of the respective product from the deuterated derivative, *does not represent a single, or single reaction, isotope effect*. They suggest that the observed k_H/k_D is a composite effect made up and determined by different isotope effects of different reaction steps; and specifically, is determined by the DIE's of the individual products, and in proportion to the yields of the latter. These features and the DIE's of the Table suggest that the "true" *α*-isotope effect in our system is not the observed effect of 1.121, but has values ranging from 1.193 down to 1.103. In this case, the aforementioned discussion and trends of the DIE's concern the "true" *α*-isotope effects themselves. The observed trends, it is significant to note, are "reasonable" being in line with the accepted understanding that *α*-isotope effects increase as the extent of rearside bonding to the *α*-carbon in the transition state decreases. Thus, *e.g.*, olefin formation is associated with higher DIE's than the substitution products are, *e.g.* 1.178 for *cis*-2-octene *vs* 1.107 for 2-octanol.

The present findings may prove to be quite significant and to have numerous implications. By being "reasonable" and internally consistent, the present DIE's and their interpretation, just as our earlier studied *β*-DIE's[1b] in the same system, offer some support to the assumption that rate and product determining steps should be treated as being the same, at least in this system. This position is of course not very well in line[1b] with the mechanism of a rate determing formation of a tight ion pair covering this solvolysis and singly responsible for the observed *α*-isotope effect, but the latter mechanism is not well accepted[6] any way. The present findings point also to a need for some reservations about mechanistic assignments[2] based on *α*-isotope effects in terms of their percent of the maximum effect of 1.22. This follows from the fact that the present work suggests the possibility that trends observed in *α*-k_H/k_D's, as the medium or other factors are varied, may actually be reflecting to a smaller or larger extent differences in product yields and not differences, or differences only, in the "true" isotope effects. Thus, it may be that some *α*-isotope effects reported in the literature may not be the isotope effects for the substitution reactions and their mechanisms which they are believed to be. For example, formation of olefins and a change in their yield, such as a possible increase of this yield in going to less nucleophilic media,[7] could possibly account for at least a part of the respective trends in the *α*-isotope effects, such as some increases in these effects observed in going to more aqueous ethanol-water mixtures or from these media to the respective trifluoroethanol-water mixtures,[2] *even if* the isotope effect (DIE) for the substitution reaction itself did not change, or did not change as much as that observed for the overall reaction. The latter isotope effect would still increase with increasing olefin yield if the DIE's of the olefins were higher than those of the substitution products, as is the case in our system (Table I), and provided that the overall α-isotope effect would depend on the relative product yields and their respective DIE's. Such a dependence is suggested by the kinetic nature assigned to the DIE's and the use of equation (4).

Thus, the present work points to the potential significance, and suggests the need for further studies, of dissected α-deuterium effects. For among other reasons, α-deuterium effects having been discussed extensively and interpreted successfully in the context of Winstein' ion pair scheme have in return provided support for this widely accepted scheme and its various mechanisms involving different rate determining steps.[2] If, however, our views about the ionization hypothesis and resulting solvolytic mechanisms,[3] which cover Winstein's scheme also, are valid, and in view of some other questions raised[6] about the prevailing interpretation of some α-deuterium effects,[2] a reexamination of the above mutual support between α-deuterium effects and Winstein's scheme may prove to be fruitful. To this end, the suggested dissection of isotope effects may be most helpful, as our present and earlier[1] work on DIE's implies. We are working along these lines.

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