STERIC EFFECTS IN HIGHLY CONGESTED SYSTEMS. STERIC RETARDATION IN THE ACID

CATALYSED DEHYDRATION OF ALKYL-DI-t-BUTYLCARBINOLS IN ANHYDROUS ACETIC ACID :

COMPARISON WITH P-NITROBENZOATE SOLVOLYSIS.

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Steric acceleration due to relief of strain in the ionisation process has been reported in the solvolysis of tertiary carbinyl p-nitrobenzoates (p-NB's)[1,2] and chlorides.[3a] The absence of any correlation between the rates and the extent of product rearrangement in the solvolysis of a series of p-NB's from tri-t-butylcarbinyl to tri-neopentylcarbinyl[2] is considered to rule out neighbouring alkyl group participation as a factor contributing to the high solvolysis rates of certain compounds. In a recent publication, Schleyer et al.[4] reported that the reactivity (log k) in a series of 2-alkyladamantyl p-NB's increased linearly with the computed hydrocarbon-cation strain energy change.

In contrast to these results, during our work on the dehydration of tertiary alcohols,[5] $R'CH_2(t-Bu)_2COH$, we were struck by the marked unreactivity of those alcohols with the most sterically demanding substituents. We wish now to report the results of a kinetic study of the sulphuric acid catalysed dehydration of alcohols I in anhydrous acetic acid. In the dehydration of I-Me, heterolysis of protonated alcohol is the rate determining step[6] since, in a virtually anhydrous system, return of the carbonium ion II to alcohol is strongly disfavoured relative to deprotonation or rearrangement to the more stable ion III. For the other alcohols the same mechanism must apply : direct comparison of alcohol dehydration and ester solvolysis should therefore be possible.
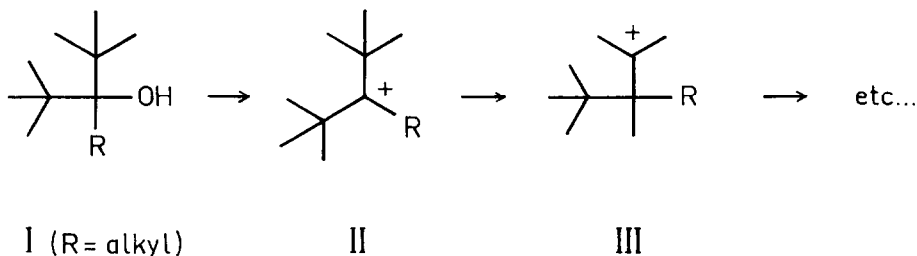

I (R = alkyl)   II   III

TABLE. — Rate constants[7] (in sec^{-1}) for the dehydration of I in anhydrous acetic acid at 25° and for the solvolysis of the corresponding p-NB's in dioxan/water at 40° (60-40 w/w ; 0.1 M $LiClO_4$) and in acetic acid at 60° (0.01 M NaOAc).

R	$-E_s$	$\Delta \log k_{OH}$ [a]	$10^5 k_{OH}$ ($H_o = -1.0$)	$10^5 k^{DW}_{p-NB}$	$10^5 k^{HOAc}_{p-NB}$
Me	0.00	0.00	39.5	0.164 [b]	1.73 [b]
Et	0.07	0.01	39.9	2.01 [b]	22.4 [b]
n-Pr	0.36	0.19	62.0	2.24 [b]	28.7 [b]
i-Pr	0.47	0.20	64.9	2.42 [c]	-
n-Bu	0.39	0.26	73.4	-	-
i-Bu	0.93	-1.05	3.48	2.63 [b]	44.7 [b]
t-Bu	1.54	-1.07	3.38	9.80 [d]	-
i-Am	0.35	0.26	73.3	-	-
neopentyl	1.74	-1.43	1.47	14.1 [d]	258 [b]
neohexyl	0.34	0.22	68.3	-	-

[a] $\Delta \log k_{OH} = \log k^R_{OH} - \log k^{Me}_{OH}$: mean value for $H_o = -0.21$ to -1.35,

[b]   determined by the spectroscopic method[2],   [c] ref.1 ,   [d] ref.2 .

Relative rates for alcohol dehydration in the range $H_o = -0.21$ to -1.35 are listed in the Table. Correlation of the rate data with σ^* and E_s gives a rough value of ρ^* (-3.6 ± 2.6) and a rather more reliable δ (1.33 ± 0.04). In view of the large error on ρ^* it must be considered fortuitous that it falls so close to that of tertiary carbinyl chloride solvolysis (-3.3)[3b]. The value of the steric constant, however, indicates that steric retardations (antilog δE_s) of close to 20, 110 and 200 can be attributed to the i-Bu, t-Bu and neopentyl groups, respectively.

Before concluding as to the origin of this steric effect, we shall first eliminate two factors which might have been considered important : neighbouring group assistance and the existence of steric constraints within the carbonium ion II. (i) The hypothesis that assistance is responsible for these retardations can be rejected on several grounds, amongst which : (a) neighbouring group assistance is inherently improbable in tertiary systems[3c], (b) alcohol I-Me gives 30-50% normal olefin (depending on the acidity) whereas none of the others yields more than 10% of the corresponding compound, the products being derived from the rearranged ion III by deprotonation, migration or fragmentation : there is, therefore, no correlation between product rearrangement and reactivity. (ii) Strictly speaking, it is not possible to determine the steric effects of R on C-O bond heterolysis without performing detailed calculations on the strain energies of the parent alcohol and the ion II in their various conformations. Nevertheless, it can be argued that, while the existence of steric constraints within the intermediate ion II can explain the reaction products[8], rehybridisation from sp^3 to sp^2 can only be associated with overall relief of steric strain and, consequently, with rate enhancement.
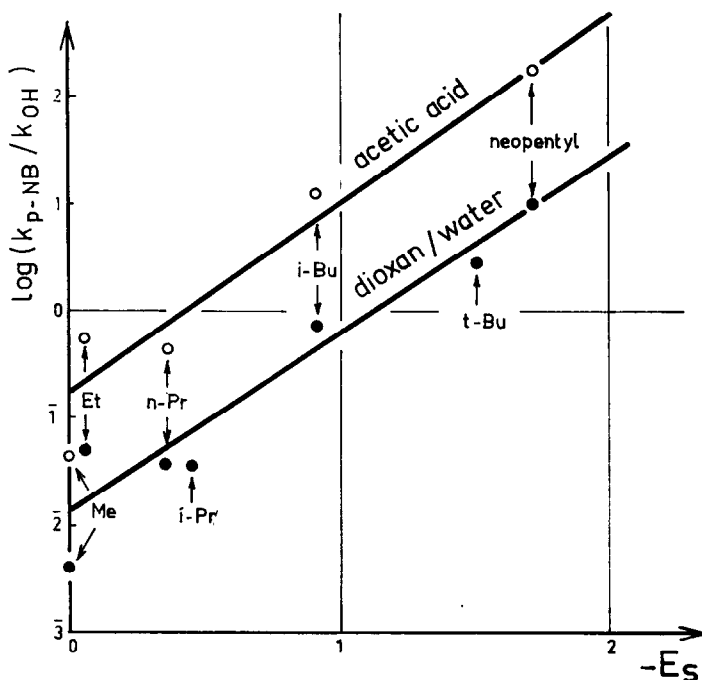
Figure.- Variation of the relative reactivites of p-NB's and alcohols, R(t-Bu)$_2$COH, expressed as a function of Taft's steric parameter E$_s$ (see Table for details)

We are led therefore to propose that a steric effect of a different nature, namely, solvent exclusion, which has already been considered in this context[2], is responsible for the retardations observed. In our view, our results are best understood in terms of a destabilisation of the transition state leading to a desolvated carbonium ion[9]. Clear-cut examples of steric hindrance to ion solvation are found in the anomalous acidities and basicities of phenols, anilines and pyridines bearing t-butyl substituents in the 2- and 6-positions[10], but its application outside this field has been rather limited[11].

If, in alcohol dehydration, steric desolvation is capable of outweighing the rate enhancing effect of B-strain relief, a third factor, so far neglected, must be responsible for the p-NB solvolysis rate enhancements[1,2]. We would suggest that the reason for the variations in the relative rates of p-NB solvolysis and alcohol dehydration, for a given tertiary carbinyl structure, lies in the contribution of the relief of front (F)-strain[12] to the reactivity of the p-NB's. In the esters the rupture of the C-O bond will be accompanied by a considerable decrease in frontal compression, whereas the separation of the water molecule, much smaller than the p-NB moiety, will be sterically of lesser importance.

The Figure shows the result of plotting log (k$_{p-NB}$/k$_{OH}$) vs. -E$_s$, data for solvolysis in dioxan/water or in anhydrous acetic acid being used. The most important feature of these plots,

apart from their approximate linearity, is that the relative rate term increases with the steric requirement of R, as would be expected. In acetic acid, p-NB solvolysis is acid catalysed so the reaction is closely analogous to alcohol dehydration, but in the comparison using p-NB solvolysis in dioxan/water neither the solvent systems nor the charge redistributions in passing from the initial state to the transition state are the same. The relative rates of solvolysis in the two media are, nevertheless, very similar. The ethyl and methyl groups lie, respectively, above and below the regression line ; this would indicate that their steric requirements in this situation are poorly described by E_s and that, in particular, the methyl group is much "smaller" relative to the other groups than is normally the case.

Further study along these lines would be invaluable to the understanding of steric effects upon the solvolysis of highly congested systems.

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(5) (a) J.S. Lomas, D.S. Sagatys and J.E. Dubois, Tetrahedron Letters, 599 (1971) ; (b) idem.
     ibid., 165 (1972) ; (c) J.E. Dubois, J.S. Lomas and D.S. Sagatys, ibid., 1349 (1971)

(6) J.S. Lomas, D.S. Sagatys and J.E. Dubois, Tetrahedron, in press.

(7) Rate constants were determined by glpc, as described for I-Me[6]. Relative rates were
     constant in the range quoted but beyond H_o = -1.35 all alcohols tended to increase in
     reactivity faster than I-Me.

(8) ref. 5a ; see also I.Ho and J.G. Smith, Tetrahedron 26 4277 (1970)

(9) In principle , both the carbonium ion and the preceding oxonium ion could be subject to
     solvent exclusion, but the effect on the latter would be less marked due to the greater
     accessibility of the charged oxygen atom ; no data on the basicities of congested alcohols
     are available.

(10) C.H. Rochester and B. Rossall, J.Chem.Soc., B, 743 (1967), and references therein.

(11) For an important exception, see W.M. Schubert and D.F. Gurka, J.Amer.Chem.Soc., 91 1443
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