PRIMARY AND SECONDARY KINETIC ISOTOPE EFFECTS
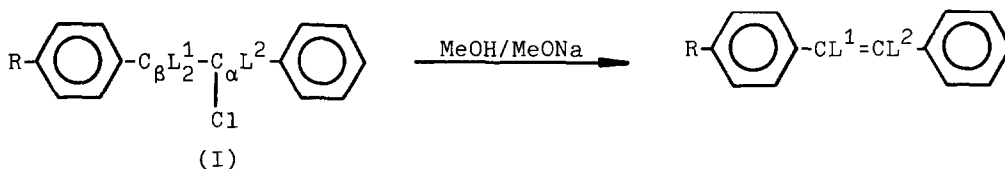## IN E2 ELIMINATION REACTIONS[1]

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Summary: Primary and secondary deuterium kinetic isotope effects have been
measured for elimination of LCl (L = H or D) from some substituted
1,2-diaryl-1-chloroethanes. Although changes in these effects are in
agreement with theoretical predictions, the high values of $(E_H-E_D)_\beta$ and
the significantly low A_H/A_D may suggest that either proton tunnelling or
an internal return mechanism is complicating this E2 elimination.

We have studied the kinetics of LCl elimination from (I) in MeOH/MeONa
in an effort to obtain an evidence for the Westheimer effect[2]. Considering
the wide range of conflicting results reported[3-5] with respect to the
interpretation of primary isotope effects $(k_H/k_D)_\beta$ in terms of transition
states (TSs) geometries, we have also estimated the secondary isotope effects
$(k_H/k_D)_\alpha$ in reactions of (I) in order to obtain information about the
rehybridization of C_α in TSs.

Mass spectroscopy showed that deuteration on C_α or C_β is $\geqslant$ 95%.
These reactions gave trans-4-substitutes stilbene in good yield (98-102%),
and rates of elimination were determined by following rates of chloride ion
accumulation by an electrometric method[6]. Results are summarized in table 1.

$$R-\langle\bigcirc\rangle-C_\beta L^1_2-\underset{\underset{Cl}{|}}{C_\alpha} L^2-\langle\bigcirc\rangle \xrightarrow{\text{MeOH/MeONa}} R-\langle\bigcirc\rangle-CL^1{=}CL^2-\langle\bigcirc\rangle$$

(I)

<u>Where:</u> $L^1 = L^2 = $ H or D; $L^1 = $ H, $L^2 = $ D; and $L^1 = $ D, $L^2 = $ H.
       R = O_2N-, Cl-, H-, H_3C-

Hammett plots, using $\sigma^-_{NO_2}$, gave reasonable straight lines with a range of ρ values $\simeq$ +1.9 ($L^1 = $ D) and $\simeq$ +2.3 ($L^1 = $ H) which can be compared with ρ value of +2.26 obtained for EtOH/EtONa catalyzed elimination from (I)[7]. A slightly more positive value, +2.5, was found for elimination from some phenylethyl chlorides[8]. Thus, neither did the change in base strength nor the introduction of an extra α-phenyl group drastically change the carbanionic character of C_β in TS. However, it is interesting to note that the deuterium substitution on C_β made the TSs more reactant-like[9], which is in accord with an E2 mechanism having a paenecarbanion TSs. This was further confirmed by the absence of exchange of hydrogen atoms on C_β of (I) under all conditions, which is also indicative of the minimal contribution of solvent effects to $(k_H/k_D)_\beta$. Thus, the increase in $(k_H/k_D)_\beta$ with the change in the electronic nature of R from O_2N- to H_3C- group may appear as a straight forward Thornton-behaviour. Accordingly, the TSs tends to be more reactant-like in the direction $O_2N->$ Cl-> H-> H_3C- . That the O_2N- analogue has the least C_β-H bond cleavage in TS, is indicated by the high $(K_H/k_D)_\beta$ = 8.8, a situation where the C_β proton is approximately half transfered to the base in the TS. For the other substituents, the proton in question would be more than half transfered, i.e., TSs with advanced C_α-Cl bond cleavage and concurrent accumulation of the negative charge on C_β. This conclusion gained some support from the observation that $(k_H/k_D)_\alpha$ increased with the increase in the electron repelling character of R. Thus, (I) at R = H_3C- would have more π-bonding between C_α and C_β than would (I) at R = O_2N- in the TS. Also, the small but significant increase in $(K_H/k_D)_\beta$ with deuterium substitution on C_α is in agreement with Thornton's prediction[4] i.e., electron repelling groups at C_α will shift TS to more reactant-like.

   The above discussion is in obvious agreement with the conclusions reached earlier by several authors[4,9]. Nonetheless, examining the enthalpies of activation and the preexponential factor, A_H/A_D, is perplexing,

especially that these authors[4,9] did not attempt investigating those constants. The high zero-point energy difference, $(E_H - E_D)_\beta \approx 13$ k J mol^{-1} with the highest value at R = H_3C- and the abnormally low A_H/A_D may be indicative of proton tunnelling[10]. Considering that tunnelling is normally associated with high k_H/k_D values[11], it is indeed puzzelling that the 4-methyl analogue, with the lowest $(k_H/k_D)_\beta$, showed the highest deviation from theoretical limits. Internal return mechanism without H/D exchange on C_β is a plausible mechanism to account for this anomaly at R = H_3C- . In this context it is irrelevant to discuss primary deuterium isotope effects in terms of TSs structure. The energies of activation show TSs with reactant-like relations different from that concluded from kineitc isotope effects. Within the experimental uncertainty, one may regard the energies of activation of the four compounds to be of the same magnitude. This situation is as peculiar as that observed by Blackwell et al.[5] who obtained a reasonable change in enthalpies of activation without substantial change in k_H/k_D values[5], for base catalyzed elimination from phenylethyl bromides and dimethyl(phenyl)sulphonium bromides.

In conclusion, care must be taken in relating kinetic isotope effects to transition states geometries[4], even for systematic changes within the same system, particularly if proton tunnelling[10] or other factors[12] are feasible.

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Table 1

Rate coefficients for methoxide promoted LCl elimination from (I) at 25°C.[a]
Rates (10^5 k_2 l mol^{-1} min^{-1}) and energies of activation (E k J mol^{-1}).

R^b	$H_\alpha H_\beta$	$D_\alpha H_\beta$	$D_\beta H_\alpha$	$D_\alpha D_\beta$	$(k_H/k_D)_\beta$	$(k_H/k_D)_\alpha$	$EH_\alpha H_\beta$	$ED_\beta H_\alpha$	$(A_H/A_D)_\beta$
O_2N-	10370.67	9564	1177.33	1050.67	8.8	1.08	85.7	97.4	0.08
Cl-	28.93	23.67	6.33	4.67	4.56	1.22	72.7	84.8	0.03
H	17.33	13.33	5.67	4	3	1.3	96.6	108.4	0.03
H_3C-	8.07	5.67	3.93	2.67	2.1	1.375	77.8	97	0.001

[a] Rate constants are accurate to $\pm$ 2%. Uncertainty in energies of activation is $\pm$4.2 k J mol^{-1}.

[b] $[I]$ = 5 x 10^{-3} mol l^{-1}; $[MeONa]$ = 7.5 - 15 x 10^{-2} mol l^{-1}.