

Rate Enhancements and Secondary β -Deuterium Kinetic Isotope Effects as Criteria of Neighbouring Group Participation. Solvolysis of Some Tertiary Alk-5-enyl Chlorides

Mirko Orlović,^a Krešimir Humski,^a Stanko Borčić,^{*a} and Eugenio Polla^{*b}

^a Faculty of Pharmacy and Biochemistry, University of Zagreb, A. Kovačića 1 41000 Zagreb, Yugoslavia

^b INA—Research & Development, Proleterskih brigada 78 41000 Zagreb, Yugoslavia

Rate enhancements in solvolysis of several of the title compounds are small or zero but significantly reduced secondary β -deuterium kinetic isotope effects indicate participation of the double bond.

It is widely recognized that in solvolyses only large rate enhancements can be taken as a valid proof of neighbouring group participation.¹ Small rate effects are considered at best ambiguous and are even taken as indicative of lack of participation.² In the simplest case, the observed rate constant ($k_{\text{obs.}}$) in the reaction of the participating system is considered to be the sum³ of the rate constant for the nucleophilically unassisted process (k_c) and of that for the anchimerically assisted reaction (k_A): $k_{\text{obs.}} = k_c + k_A$. In order to estimate k_A , the rate constant of a reference substrate is set equal to k_c which is in general a valid approximation only if $k_A \gg k_c$. When however $k_c \approx k_A$ the observed rate ratios (substrate/reference) are small but can conceal considerable participation.⁴

We have measured the solvolysis rates of several tertiary alk-5-enyl chlorides (k_u) and those of the corresponding saturated analogues (k_s). The results are given in Table 1. As

can be seen the observed rate enhancements (k_u/k_s) are either non-existent or very moderate. It is tempting to conclude that [with perhaps the exception of (3)] none of these chlorides solvolyses with the participation of the double bond.

Secondary β -deuterium kinetic isotope effects (β -KIE) are very sensitive probes for neighbouring group participation.⁵ Their magnitude is drastically reduced by anchimeric assistance. Examples include *inter alia* the solvolyses of [1,1,1-²H₃]-5-methoxy-2-pentyl⁶ and [2,2-²H₂]-4-methoxypentyl *p*-bromobenzenesulphonate,⁶ [2,2-²H₂]-1-aryl-5-methylhept-5-enyl chloride,⁷ [2,2-²H₂]-1-phenyl-4-methoxybutyl chloride,⁸ [4 β -²H]-3 β -cholesteryl toluene-*p*-sulphonate,⁹ [2,2,4,4-²H₄]-cyclobutyl¹⁰ and 1-([²H₃]methyl)cyclobutyl methanesulphonate,¹¹ and [3,3-²H₂]-2-*exo*-norbornyl *p*-bromobenzenesulphonate.¹²

As a further test for possible participation we have prepared and measured the solvolysis rates of tertiary chlorides (3)—(6)

Table 1. Solvolysis rates and secondary β -deuterium kinetic isotope effects of some tertiary alk-5-enyl and alkyl chlorides (80% aq. ethanol at 50.0 °C).

Compound ^a Cl(CD ₃) ₂ CR	k_u/k_s ^b	k_H/k_D ^c
(1) ^d R = Et	—	1.79(3) ^e
(2) R = [CH ₂] ₃ Bu ^s	—	1.80(3)
(3) R = [CH ₂] ₃ C(Me)=CHMe	18.9	1.37(3)
(4) R = [CH ₂] ₃ C(Me)=CH ₂	1.63	1.22(3)
(5) R = <i>cis</i> -[CH ₂] ₃ CH=CHMe	0.75	1.72(4)
(6) R = [CH ₂] ₃ CH=CH ₂	0.78	1.57(2)

^a The rates of the corresponding protio analogues are ($\times 10^{-4}$ s⁻¹): (3) (33.0 \pm 0.1); (4) (3.79 \pm 0.11); (5) (1.94 \pm 0.04); and (6) (2.10 \pm 0.05). ^b Rate ratio of the protio compounds: k_u is the rate constant of the unsaturated chloride, k_s that of the corresponding saturated chloride. ^c The uncertainty of the last reported figure (standard deviation of the mean) is shown in parentheses. ^d In solvolysis of this compound elimination is not part of the rate determining step, *i.e.* there is no contribution of a primary isotope effect to the reported k_H/k_D . See ref. 13. ^e At 25.0 °C. Ref. 13.

with two deuteriated methyl groups. The observed β -KIE are shown in Table 1 (k_H/k_D). As can be seen alk-5-enyl chlorides (3), (4), and (6) solvolyse with significantly reduced β -KIE relative to those measured with the saturated chlorides (1) and (2). A striking case is that of (6) where a rate deceleration is observed but the magnitude of β -KIE indicates some participation of the double bond.

Thus even if reference substrates are chosen with utmost care, a lack of rate enhancement in solvolysis does not necessarily signify a lack of neighbouring group participation.

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