Tetrahedron Letters No. 56, pp. 4913-4915, 1969.   Pergamon Press.   Printed in Great Britain.

MECHANISMS OF ELIMINATION REACTIONS. PART 2.[1] AN ALTERNATIVE INTERPRETATION OF THE RATIO $\underline{k}_{OTs}/\underline{k}_{Br}$ FOR BIMOLECULAR ELIMINATION IN THE 2-PHENYLETHYL SERIES

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(Received in UK 24 September 1969; accepted for publication 30 October 1969)

Since DePuy and Bishop first noted that the relative reactivity of alkyl tosylates and their corresponding bromides was greatly dependent on the reaction, and its conditions,[2] the ratio $\underline{k}_{OTs}/\underline{k}_{Br}$ has been used on a number of occasions as a means of assessing the extent of C-X bond breaking in the transition state of substitution and elimination reactions.[3-5] For S_N1 reactions, in which C-X bond breaking is extensively advanced in the transition state, $\underline{k}_{OTs}/\underline{k}_{Br}$ is large, as the developing charge is more effectively delocalised by the toluene-*p*-sulphonate anion.[3] However, for S_N2 reactions with powerful nucleophiles, especially in dipolar aprotic solvents, or for E2 reactions, values of $\underline{k}_{OTs}/\underline{k}_{Br}$, which are small and in some cases less than unity, have been observed.[3] In these cases, C-X bond breaking is less advanced and the beneficial delocalising ability of the developing toluene-*p*-sulphanate anion is outweighed by the greater polarisability of the C-Br bond.[5c] Within this framework, it has been suggested that the ratio $\underline{k}_{OTs}/\underline{k}_{Br}$ increases with increasing breaking of the C-X bond.[3]

A number of different types of kinetic evidence have been employed to give information on the nature of the transition state which is involved in bimolecular elimination in the 2-phenylethyl series. The Bronsted components β, for elimination from 2-*p*-nitrophenylethyl and 2-phenylethyl bromides with substituted phenoxides are 0.67 and 0.54, respectively.[6] As might have been predicted, these values suggest that electron withdrawing aromatic substituents increase the extent of C_β-H bond breaking in the transition state. In both *t*-butyl alcohol and ethanol containing their corresponding lyate ions, an increase in $\underline{k}_{OTs}/\underline{k}_{Br}$ with increasing electron withdrawing power of the aromatic substituent is also observed (see Table 1). Consequently, it has been proposed that increased C_β-H bond breaking induces increased C_α-X bond breaking and the ElcB mechanism is paradoxical.[4] Considering an E2 reaction as an internal nucleophilic displacement, in support of the above proposition, it could be argued that an increase in the electron withdrawing nature of the substituent causes greater delocalisation of the charge on the beta-carbon, thus producing a less active nucleophilic centre. Although such an argument would be reasonable for an ElcB mechanism,[7] the increased extent of partial carbanion formation in the E2 reactions could outweigh the greater delocalisation by a more electron withdrawing substituent. In any case, two peculiar features of the above results warrent further comment.

In the first place, it is surprising that electron withdrawing substituents apparently promote ionisation of the C_α-X bond. Secondly, as $\underline{k}_{OTs}/\underline{k}_{Br}$ is larger in *t*-butyl alcohol than in ethanol, C_α-X bond breaking appears to be more advanced in the poorer solvating medium. Although it could be argued that the charge density of the beta-carbon is reduced by greater delocalisation into the C_α-X bond in *t*-butyl alcohol, such an explanation is in conflict with the Hammett reaction constants, which suggest much greater carbanion character for the eliminations from the tosylates in the less polar solvent (ρ = 3.4 (*t*-BuOH) and 2.3 (ethanol)).[2] In both cases, measurements of primary kinetic hydrogen isotope effects suggest transtition states in which the proton is approximately half transferred to the base.[7] Consequently any increase in carbanion character must arise from a decrease in C-X bond breaking in the less polar medium.

An alternative interpretation of the ratio k_{OTs}/k_{Br} avoids the discrepancy in conclusions from different experimental approaches. A complete understanding of the ratio requires a knowledge of its value when no C-X bond breaking occurs in the transition state. For this circumstance, the relative reactivity is dependent on the electrophilic nature of the carbon atom. The four electronegative atoms of the tosylate group should be more electron with-drawing than the single halogen (a prediction which is supported by σ^* values of 1.31 (OTs) and 1.00(Br)[9]) and for no bond breaking, a value of k_{OTs}/k_{Br} of slightly greater than unity is expected.[10] A gradual increase in bond breaking will cause a decrease in the ratio until it is dominated by polarisability considerations. Further increases in bond breaking then produce a rise in k_{OTs}/k_{Br} as the charge delocalisation factor gains in importance.

Within the bounds of this alternative explanation, the low value for the 2-*p*-anisyl substrates in ethanol reflects transition states in which C-X bond breaking is presumably near the minimum in Figure 1, and in the remaining cases C-X bond breaking is less developed and a trend towards greater carbonion character is exhibited. The secondary α-deuterium isotope effects for elimination from a series of substituted 2-phenylethyl tosylates support this conclusion (Table 1). These effects arise mainly from a change in hybridisation at the alpha carbon in attaining the transition state.[11] As C-X bond breaking increases, the hybridisation at the alpha carbon progresses more towards the sp^2 extreme and the value of the secondary isotope effect increases. Consequently C-X bond breaking is more advanced in the case of the p-methoxy-compound than the p-chloro-substrate. Values of k_{OTs}/k_{Br} which are small or less than unity may thus be ambiguous and should not be used as the only source of mechanistic criterion.

<u>Table 1</u> The ratio k_{OTs}/k_{Br} for E2 reactions of some 2-Y-phenylethyl substrates at 30°

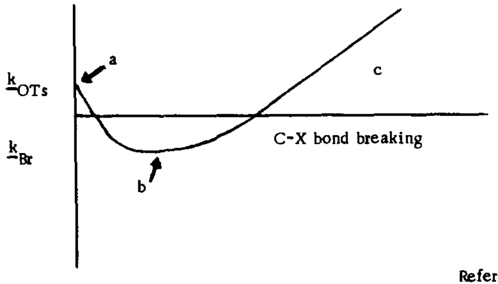
Y	Solvent	base	k_{OTs}/k_{Br} [4]	$k_{YC_6H_4CH_2CH_2OTs}/k_{YC_6H_4CH_2CD_2OTs}$ ‡
p-OCH$_3$	EtOH	$\bar{\text{O}}$Et	0.065	
H	EtOH	$\bar{\text{O}}$Et	0.10	
*p*OCH$_3$	*t*-BuOH	*t*-$\bar{\text{O}}$Bu	0.15	1.047 ± 0.004*
H	*t*-BuOH	*t*-$\bar{\text{O}}$Bu	0.22	1.043 ± 0.004
p-Cl	*t*-BuOH	*t*-$\bar{\text{O}}$Bu	0.44	1.017 ± 0.005
m-Br	*t*-BuOH	*t*-$\bar{\text{O}}$Bu	1.19	
p-NO$_2$	*t*-BuOH	*t*-$\bar{\text{O}}$Bu	1.57	

‡ Each rate constant (calculated by a least squares procedure) measured three or four times.

* Average ratio with standard deviation obtained be permutating each rate constant for the hydrogen compound with each for the

dideutero substrate.

Figure 1 The anticipated profile of $\underline{k}_{OTs}/\underline{k}_{Br}$ against extent of C-X bond breaking



$\underline{k}_{OTs}/\underline{k}_{Br}$ is dominated in the following regions by:-

a. The electron withdrawing power of X

b. The polarisability of the C-X bond

c. The delocalising ability of X^-

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