

HYDROGEN-DEUTERIUM ISOTOPE EFFECTS FOR
THE BASE PROMOTED E2 REACTION OF QUATERNARY
AMMONIUM IONS. THE EFFECT OF BASE, SOLVENT,
AND STRUCTURE ON THE NATURE OF THE
TRANSITION STATE.¹

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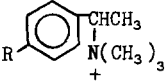
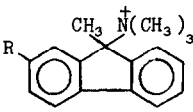
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In a recent publication² the mechanism of the reaction of 1-arylethyltrimethylammonium ions with ethoxide ion in ethanol at 70° was shown to be E2. The transition state for this process involved extensive proton transfer to base as exhibited by the observed trend in hydrogen-deuterium isotope effects^{3,4,5} with variation in para-substituent as well as the observation of a positive Hammett rho value of +0.95.

In order to gain an insight into the effect of base and solvent on the nature of the transition state for an E2 process, we have determined the hydrogen-deuterium isotope effects as well as the Hammett rho for reaction of the 1-arylethyl salts with t-butoxide in t-butanol at 30° and ethoxide ion in EtOH-DMSO mixtures at 70°. These results are shown in the Table along with the results obtained previously² for reaction with ethoxide ion. The effect of a structural change on the nature of the transition state was investigated by studying the reaction of 2-substituted 9-methylfluorene-9-trimethylammonium ions with ethoxide⁶ at 40° and the results are shown in the Table.

The effect of solvent in determining the nature of the transition state for the reaction of the charged substrate with ethoxide was determined by varying the solvent composition from 100 vol. % EtOH to 40 vol. % EtOH-DMSO. It is seen from the results in the Table that, whereas the

rate constant is increased by a factor of 18 for the unsubstituted compound when DMSO is added⁷, the value for k^H/k^D and ρ remain essentially constant. The transition state must therefore not be appreciably affected by a change in solvent composition or the values of k^H/k^D and ρ are insensitive under our particular conditions. It is of interest to note that for reaction of a neutral substrate, benzyl nitrate with ethoxide ion in EtOH-DMSO mixtures⁸, it was also concluded that the transition state geometry was insensitive to changes in solvent composition.

Substrate	R	Base/Solvent	$k_2 \times 10^4$ ^a	T°C	(k^H/k^D)	ρ ^b
	OCH ₃	EtO ⁻ /EtOH	2.14	70	4.35±0.10	
	H		2.59		4.46±0.04	+ 0.95
	CF ₃		9.51		4.84±0.13	
	H	EtO ⁻ /50 vol. % EtOH-DMSO	24.8	70	4.22±0.12	+ 1.03
	CF ₃		109.		4.72±0.14	
	H	EtO ⁻ /40 vol. % EtOH-DMSO	46.1	70	4.27±0.11	
	H	t-BuO ⁻ /t-BuOH	30.4	30	5.68±0.04(4.63) ^c	+ 0.98
	CF ₃		100.		6.39±0.26(5.15) ^c	
	H	EtO ⁻ /EtOH	14.9	40	4.21±0.10(3.71) ^c	
	I		28.5		5.66±0.21(4.86) ^c	+ 0.86
	Br		33.5		6.17±0.25(5.26) ^c	

^aIn l. mole⁻¹ sec.⁻¹ ^bThe ρ value was obtained by measuring the rate constants for at least four substituted compounds. k^H/k^D at 70° calc. from the value obtained at the lower temperature.

The hydrogen-deuterium isotope effect and ρ was determined for the reaction of two 1-arylethyl ions with t-butoxide in t-butanol at 30°. This increase in the strength of the abstracting base when one goes from ethoxide ion in ethanol to t-butoxide in t-butanol⁹ is reflected in the magnitude of the respective rate constants. It is reasonable to conclude that the small but significant increase in the magnitude of k^H/k^D when one changes the abstracting base from ethoxide to t-butoxide is a result of a more reactant-like transition state as predicted by Thornton⁴ with the proton more than one-half transferred to base³. However, it is noteworthy that the increase in rate¹⁰ when the abstracting base is made stronger has only a minor effect on the magnitude of the isotope effect; i.e. 4.46 (calc.) and 4.63 at 70° for ethoxide and t-butoxide,

respectively, for the unsubstituted compound. A similar trend is also observed for the p-CF₃ substrate. Consequently, it appears that for this system, the transition state geometry is very little affected by a change in the basicity of the reaction medium. Further evidence to support this conclusion is that the value for rho remains constant for reaction in the two solvent systems.

The insensitivity of the H/D effect to strength of the abstracting base is particularly significant when it is noted that k^H/k^D varies to a much greater extent when the para-substituent is varied, see Table for results in the two base/solvent systems, although the rate constant is not affected to nearly the same degree. For our system, therefore, it appears a change in electron-withdrawing or donating ability of the para-substituent of the substrate is much more important in determining the structure of the transition state than variation in the strength of the abstracting base.

The effect of a change in structure of the reactant was examined by studying the reaction of several 2-substituted 9-methylfluorene-9-trimethylammonium ions with ethoxide in ethanol at 40°. The rate constant results, as shown in the Table, show that this reaction is considerably more facile than that of the 1-arylethyl salts which suggests that the transition state for reaction of the fluorenyl compounds has considerably more double-bond character¹¹ since the acidity of the β -hydrogen in the two systems is expected to be similar. The value of rho, however, remains essentially unchanged. The proton is more than one-half transferred to base at the transition state since the variation in the magnitude of the isotope effects with the Hammett σ value of the substituents is in accord with prediction^{11,3}.

A plot of $\log (k^H/k^D)$ ¹² at 70° versus the Hammett σ constants is shown in the Figure for the ethoxide promoted reaction of several ring substituted compounds derived from the two substrates under discussion. It is noted from the slope of the plots that the effect of substituent on the variation in the magnitude of k^H/k^D is markedly less for reaction of the 1-arylethyl salts than for the 9-methylfluorene-9-trimethylammonium ions even though the Hammett rho values are very similar. It appears, therefore, that a comparison of hydrogen-deuterium isotope effects in terms of the degree of C-H bond weakening is valid only within a particular reaction series¹³. We plan to determine the nitrogen isotope effects associated with reaction of the two substrates in various base/solvent conditions since the interpretation of this isotope effect is considered to be more straightforward than that of the H/D effect.

References

1. The financial assistance of the National Research Council of Canada is gratefully acknowledged.
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4. E.R. Thornton. *J. Amer. Chem. Soc.* 89, 2915 (1967).
5. R.A. More O'Ferrall. *J. Chem. Soc. B.* (1970).
6. The mechanism of this reaction was shown to be E2 using the procedures described in ref. 2.
7. The effect is presumably due to the ability of DMSO to desolvate the base, ethoxide.
8. C.A. Pollock and P.J. Smith. *Can. J. Chem.* 49, 3856 (1971).
9. See K. Bowden. *Chem. Rev.* 66, 119 (1966) for values of the H- function.
10. One must take into account that the rate constants were measured at different temperatures.
11. G.S. Hammond. *J. Amer. Chem. Soc.* 77, 334 (1955).
12. Calculated from values at 40° for fluorenyl compounds.
13. This is in agreement with the conclusion of A.J. Kresge, D.S. Sagatys and H.C. Chen. *J. Amer. Chem. Soc.* 90, 4174 (1968).

