# The Reaction of 9-Fluorenylmethanol with Base: a Carbanion Mechanism of β-Elimination

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Summary In aqueous solution, base-catalysed β-elimination of 9-fluorenylmethanol is accompanied by reversible formation of a carbanion, which is shown to be an intermediate.

At 25°, in aqueous sodium hydroxide, β-elimination of 9-fluorenylmethanol (I), to form dibenzofulvene, occurs by an *ElcB* mechanism.[1] Rate constants for elimination, k_E,

$$OH^- + RCL \cdot CH_2 \cdot OH \xrightarrow{k_2} RC{=}CH_2 + OH^-$$
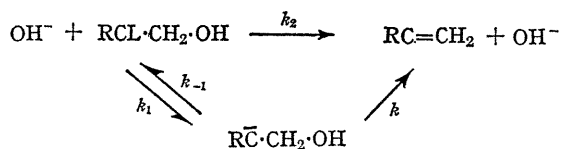
RCH$_2$ = Fluorene; (I-*h*) L = H; (I-*d*) L = ^{2}H; (I-*t*) L = ^{3}H

and for β-hydrogen exchange, k_x, were determined respectively by spectrophotometry and liquid scintillation counting. In terms of the scheme, which combines the possibilities of elimination by both *ElcB* and *E2* mechanisms, $k_x = k_2 + k_1$ and $k_E = k_2 + \alpha k_1$, where $\alpha = k/(k + k_{-1})$. Two pieces of evidence indicate that a carbanion is formed in the course of reaction: (i) The rate of tritium exchange of (I-*t*) slightly exceeds that of elimination from (I-*h*); (ii) Elimination of (I-*h*) in D$_2$O, and of (I-*d*) in H$_2$O, showed kinetic induction periods which could be interpreted quantitatively in terms of isotopic exchange.

A kinetic analysis of the induction periods led to identification of the carbanion as a reactive intermediate. For the reaction of (I-*h*) in D$_2$O, the analysis yields the rate constants k_E^H and k_E^D for elimination of (I-*h*) and (I-*d*), and the rate constant k_x^H for exchange of (I-*h*), the isotopic form of the substrate initially present. In terms of the pseudo-first-order kinetic plots shown in the Figure, k_E^H and k_E^D clearly correspond to the initial and limiting slopes of the curve for D$_2$O. Although the origin of k_x^H is less easily seen, it is related, together with k_E^H and k_E^D, to the fraction of net elimination occurring prior to completion of exchange.

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The mechanism of elimination can be determined by comparing the isotope effect upon elimination, k_E^H/k_E^D, in effects, arising from the change in base from OH^- to OD^-, and in leaving group from OH to OD.

Rate constants[a] for exchange and elimination in H_2O and D_2O at 25°

Solvent	$10^4 k_E^H$	$10^4 k_E^D$	$10^4 k_x$	k_E^H/k_E^D	$10^4 k_x^T$ (obs.)	$10^4 k_x^T$ (calc.)
D_2O	14·3	1·97	59·0[b]	7·2	3·30	3·44
H_2O	1·81	0·37	6·0[c]	5·1	2·23	2·9

[a] All rate constants are second order with units l. mole^{-1}sec.$^{-1}$; [b] k_x^H; [c] k_x^D.

the single solvent D_2O, with the *solvent* isotope effect upon elimination of (I-*h*) in H_2O and of (I-*d*) in D_2O. If the carbanion is not an intermediate, $k_2 \gg \alpha k_1$ and $k_E^H/k_E^D = k^H/k_2^D$, the primary isotope effect upon E2 elimination; while the solvent isotope effect comprises contributions, both from the primary effect k_2^H/k_2^D, and from secondary
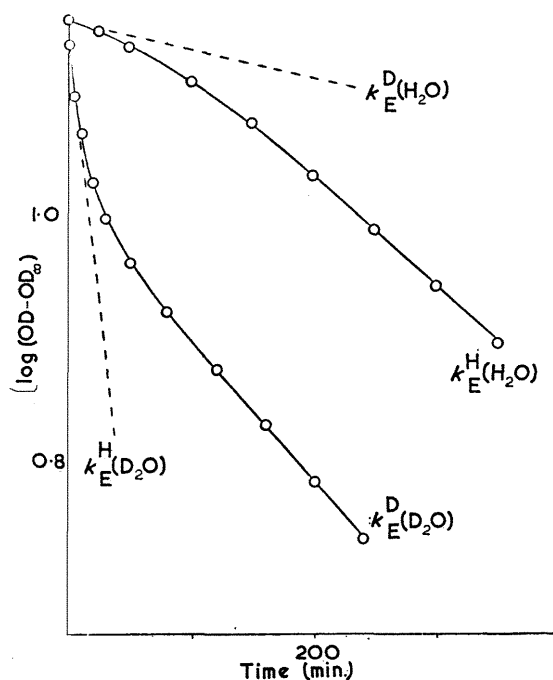

FIGURE

Plots of log(OD-OD∞) *vs.* time for reactions of isotopically substituted 9-fluorenylmethanol (I) with sodium hydroxide in H_2O and D_2O. Upper curve (I-h) in H_2O; lower curve, ⊐-d) in D_2O. Base concentrations are approximately the same. OD denotes optical density of the product.

The experimental value for the primary isotope effect is shown in the Table; for D_2O, $k_E^H/k_D^E = 7·2$. The solvent isotope effect may be determined either directly, or from the limiting slopes of the plots for H_2O and D_2O shown in the Figure, and was found to be 0·92 ± 0·03. Since secondary isotope effects are much smaller than large primary effects,[2] and in this instance probably compensating, we conclude that the observed solvent isotope effect is too small to incorporate a primary effect as large as 7·2 and, therefore, is inconsistent with an E2 mechanism. On the other hand, since reactions involving transfer of a proton in a pre-equilibrium step normally proceed faster in D_2O than in H_2O, it is quite consistent with an E1cB mechanism.

Quantitative confirmation of this conclusion comes from an examination of the rate constants for hydrogen isotope exchange. For an E1cB mechanism, $\alpha k_1 \gg k_2$ and since, for low substrate concentrations, α (the fraction of carbanion proceeding to form product) depends only upon the isotope in the solvent and not upon that in the substrate, in D_2O, $k_E^H/k_E^D = k_1^H/k_1^D$, the isotope effect upon ionization of (I). For this mechanism also, k_x^H, the rate constant for exchange of (I-*h*) in D_2O, may be identified with k_1^H, and use of the Swain Schaad relation[3] between deuterium and tritium isotope effects, $k_H/k_T = (k_H/k_D)^{1·442}$, allows calculation of the independently measured rate constant for tritium exchange, k_x^T. As shown in the Table, for D_2O, excellent agreement between calculated and observed rate constants is obtained.

For the reaction of (I-*d*) in H_2O, agreement between the corresponding calculated and observed values of k_x^T is less satisfactory and a smaller value of k_E^H/k_E^D is obtained. These discrepancies are in part due to greater intrinsic errors in the measurements for H_2O, but may indicate the presence of a component of E2 elimination, with a low primary isotope effect, contributing significantly only to the slow reaction of (I-*d*) in H_2O.

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[2] For secondary solvent isotope effects upon E2 elimination, see L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 6149.
[3] C. G. Swain, E. C. Stivers, J. F. Reuwer, jun., and L. J. Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885; E. S. Lewis and J. K. Robinson, *ibid.*, 1968, **90**, 4337.