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Borderline Solvolytic Reactions. Appearance of Solvent-Promoted E2 Reaction in Competition with Stepwise Elimination and Substitution Reactions

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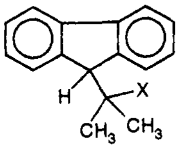
We report that a water-promoted concerted E2 reaction of 9-(1-X-ethyl)fluorene (**1**-X, X = Br or I) in 25 vol % acetonitrile in water affording 9-(1-ethylidene)fluorene (**3**) competes with stepwise substitution and elimination reactions *via* the ion pair providing 9-(1-hydroxyethyl)fluorene (**1**-OH), 9-(1-acetamidoethyl)fluorene (**1**-NHCOMe), and 9-vinylfluorene (**2**) (Scheme 1).

Solvolysis of substrates having a β-hydron usually provides elimination as well as substitution products. Frequently, the elimination and substitution reactions are carbocationic processes having a common carbocation or ion-pair intermediate.[1] More acidic substrates may undergo spontaneous, concerted, E2 elimination induced by the solvent. However, it is difficult to distinguish the solvent-promoted E2 reaction from other mechanistic alternatives, and no conclusive evidence for such a mechanism seems to have been reported previously.[1]

Recently, the tertiary substrates 9-(2-X-2-propyl)fluorene (**4**-X, X = Br, Cl, OAc, or PhOH$^+$) were shown, by the measured kinetic deuterium isotope effects, to solvolyze to intermediates common to substitution and elimination in highly aqueous acetonitrile.[2−4] Both substitution, which yields the alcohol and the amide, and elimination, which yields the terminal alkene, go through these irreversibly formed ion pairs or ion−molecule pair. The intermediate was found to be very unstable since it shows an extremely small discrimination between different nucleophiles such as water, methanol, acetonitrile, and added strong nucleophiles. The presence of strong base opens up a parallel concerted E2 reaction by abstracting the more acidic hydron to give the more stable alkene.[5] The closely related secondary substrate **1**-X used in this study would be expected to solvolyze more slowly, providing an even less stable potential ion-pair intermediate which should favor a parallel E2 reaction with the solvent.



4-X

The reaction of **1**-X (X = Br or I) at 70 °C yields **3** as the major product (69% and 95%, respectively, Scheme 1). Contrary to what was found for the tertiary substrate **4**-X, the terminal alkene **2** is formed in only trace amounts. The rates, which were measured by a sampling HPLC procedure, and the kinetic deuterium isotope effects are shown in Table 1. The latter were obtained by measuring the rates of reactions of [9-^{2}H]-9-(1-X-ethyl)fluorene and 9-([1,2,2,2-^{2}H$_4$]-1-X-ethyl)-fluorene, respectively.

Scheme 1

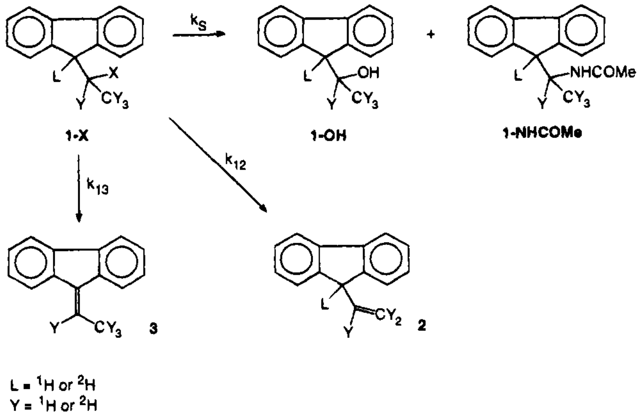


Table 1. Rate Constants and Kinetic Deuterium Isotope Effects for the Reactions of **1**-Br[a] and **1**-I[a] in 25 vol % Acetonitrile in Water

base	$10^6 k_{obs}$[b]	k_{obs}^H/k_{obs}^D	k_{13}^H/k_{13}^D	k_S^H/k_S^D	k_{obs}^H/k_{obs}^{D4}	k_{13}^H/k_{13}^{D4}	k_S^H/k_S^{D4}
			1-Br				
none[c]	33.6[e]	2.0	4.3	0.9	1.2	1.2	1.2
HO$^-$ [d]	676 × 10^3 [f]	7.5	7.5		1.3	1.3	
			1-I				
none[c]	136[e]	3.8	4.7	0.9			
HO$^-$ [d]	1.86 × 10^6 [f]	6.3	6.3				

[a] Substrate concentration 0.2 mM. [b] $k_{obs} = k_S + k_{12} + k_{13}$. [c] 70 °C. [d] 25 °C. [e] In s^{-1}, pH 2.8. [f] In M^{-1} s^{-1}.

On the basis of the following results, we conclude that the reaction which gives alkene **3** is of solvent-promoted E2 type.

(i) The large isotope effect of $k_{obs}^H/k_{obs}^D = 2.0$ at 70 °C for the reaction of **1**-Br without added base (and $k_{obs}^H/k_{obs}^D = 3.8$ for **1**-I, Table 1) shows that the reaction to give alkene **3** does not have an irreversibly formed carbocationic intermediate in common with the other reactions, since an isotope effect of $k^H/k^D \leqslant 1.15$ at 25 °C is expected for such a mechanism.[6] A reversibly formed intermediate which undergoes rate-limiting hydron transfer can be ruled out since it is unreasonable that such a short-lived ion pair would react exclusively to yield **3** at a low concentration of hydroxide anion. Accordingly, the results strongly indicate a separate reaction to alkene **3**. The isotope effects on this solvent-promoted E2 reaction are $k_{13}^H/k_{13}^D = 4.3$ and $k_{13}^H/k_{13}^D = 4.7$, respectively (Table 1).

(ii) Another independent, strong indication of a one-step mechanism for the elimination reactions of **1**-Br and **1**-I is the measured Brønsted parameters of $\beta = 0.42$ and $\beta = 0.41$, respectively (Figure 1). These large values exclude reactions through ion pairs, either coupled with the substitution reactions or as separate reactions. However, they indicate irreversible carbanion reactions (E1cB$_{irrev}$) or one-step concerted reactions (E2). Comparison with the base-promoted elimination reaction of 9-(chloromethyl)fluorene, which has been concluded to be of E2 type,[5] strongly suggests that the reactions of **1**-Br and **1**-I are E2 reactions and not E1cB$_{irrev}$ reactions. The assignment of the E2 mechanism to the elimination of HCl from the fluorene derivatives was based upon analysis of Brønsted β as a function of substrate acidity, leaving group, and α-substituents.[5] A small decrease in β for a change in leaving group from Br$^-$ to I$^-$ is predicted by the variable E2 transition-state theory.[5,7]

The catalytic constants for water as a base fall below the Brønsted lines for the acetate anions by factors of 6−8.

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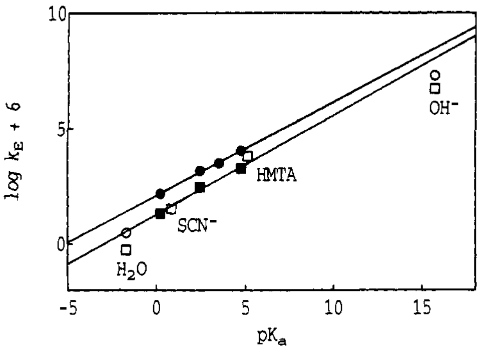

Figure 1. Brønsted plots for the solvolyses of **1**-Br (squares) and **1**-I (circles) in 25 vol % acetonitrile in water at 70 °C; ionic strength 0.75 M maintained with sodium perchlorate. The slopes, $\beta = 0.47$ and $\beta = 0.41$, respectively, are based upon the data for the substituted acetate anions (filled symbols). The pK_a values refer to water. The rate constants for hydroxide ion are extrapolated from lower temperatures. HMTA = hexamethylenetetramine.

Negative deviations of the catalytic constant for water are well-known for hydron transfer to and from carbon.[8-10] The low catalytic activity of water probably reflects some kind of solvation effect.

(iii) The sensitivity to solvent "ionizing power" is small; the Grunwald–Winstein parameters for the solvent-promoted eliminations in methanol–water mixtures are $m_E = 0.36$ (**1-Br**) and $m_E = 0.26$ (**1-I**).

It has been shown previously that E2 reaction is favored relative to stepwise solvolysis when the solvent is made less polar and when strong base is used.[1,2,5] Furthermore, it has been shown that, if there is more than one β-hydron in the substrate, the more acidic hydron is abstracted in the base-promoted E2 reactions of fluorenyl derivatives and of 2-chloro-2-methyl-1-phenylpropane.[5,11] Stepwise solvolytic elimination, on the other hand, yields the elimination product from the carbocationic intermediate which is stabilized hyperconjugatively by the β-hydrons. The β-hydron that gives the largest hyperconjugative stabilization of the intermediate is the one that is preferentially abstracted by the base (leaving group, solvent, or added base) in the stepwise solvolytic elimination reaction.[1] The conclusions of this investigation are consistent with these previous results.

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