Mechanisms of Competing Solvolytic Elimination and Substitution Reactions. The Role of Ion-pair Intermediates in Aqueous Solvents

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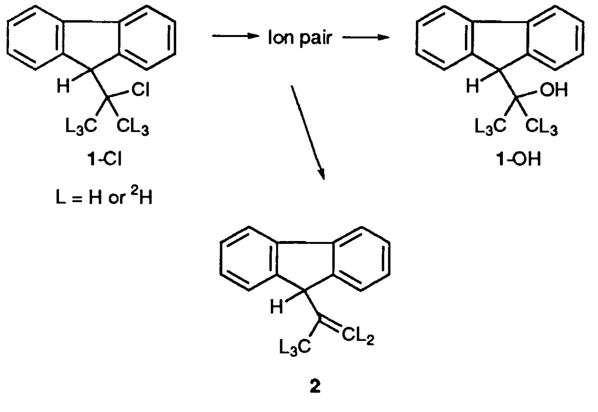
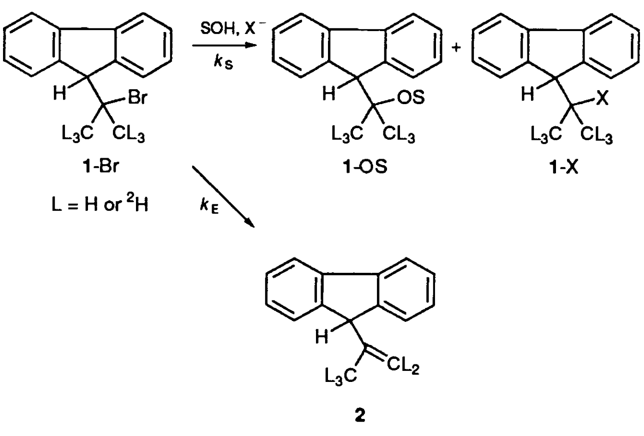
Solvolysis of 9-(2-bromo-2-propyl)fluorene **1**-Br in mixtures of water with methanol or acetonitrile at 25 °C provides the elimination product 9-isopropenylfluorene **2**, and the substitution products 9-(2-hydroxy-2-propyl)fluorene **1**-OH and 9-(2-methoxy-2-propyl)fluorene **1**-OMe. The Grünwald–Winstein parameter was measured in methanol–water mixtures as $m_{\text{obs}} = 0.70$, which is composed of the parameter for the elimination reaction, $m_E = 0.65$, and the substitution reaction, $m_S = 0.83$. The parameters for the corresponding chloride **1**-Cl were measured as $m_{\text{obs}} = 0.82$, $m_E = 0.76$ and $m_S = 0.97$. The kinetic deuterium isotope effects for the reactions of the hexadeuteriated analogue 9-(2-bromo[$^2H_6$]-2-propyl)fluorene ([$^2H_6$]-**1**-Br) were measured as $(k_E^H + k_S^H)/(k_E^{D6} + k_S^{D6}) = 2.3 \pm 0.1$ for the disappearance of the substrate in 70 vol% methanol in water, and $k_E^H/k_E^{D6} = 3.1 \pm 0.1$ and $k_S^H/k_S^{D6} = 1.4 \pm 0.1$ for the elimination and substitution, respectively. In pure acetonitrile the alkene **2** is the sole product and the isotope effect was found to be $k_E^H/k_E^{D6} = 2.3 \pm 0.1$. These results strongly indicate a branched mechanism involving rate-limiting formation of a common contact ion pair which either undergoes nucleophilic attack by the solvent or is dehydronated. The intermediate shows a very small discrimination between different nucleophiles. Thiocyanate ion and azide ion, which are assumed to react with diffusion-controlled rates with the ion pair, are only a few times more reactive than a water molecule in 70 vol% methanol in water, $k_{\text{SCN}}/k_{\text{HOH}} = 3$ and $k_{\text{N3}}/k_{\text{HOH}} = 4$, ratios of second-order rate constants. Methanol was found to be slightly less reactive than water, $k_{\text{MeOH}}/k_{\text{HOH}} = 0.7$.

It was shown recently that the solvolysis of **1**-Cl in highly aqueous acetonitrile provides the elimination and substitution products through a common carbocation ion pair (Scheme 1).[1] Evidence for such a mechanism, with rate-limiting ionization, was the measured kinetic deuterium isotope effects and the observed catalysis of the elimination reaction of the ion pair by general bases (Brønsted $\beta = 0.05$) as well as the extremely small discrimination between added nucleophiles for reaction to substitution products. The lifetime of the ion pair was estimated to be very short, $t_{\frac{1}{2}} \approx 1 \times 10^{-11}$ s,[1] employing the 'azide-clock' method.[2] Some data from product studies of the bromide **1**-Br were included in the same report.[1]



Scheme 1

In the present study we have examined the reactions of **1**-Br in more detail by measuring both rates and isotope effects. The mechanisms of these solvolysis reactions are of great interest since they are expected to be close to the borderline between one-step and multistep reactions owing to the short lifetime of the potential ion-pair intermediate 1^+Br^-. Accordingly, it has been concluded that the existence of a very short-lived carbocation (R^+) disappears in the presence of a highly efficient nucleophile (X^-).[3,4] Thus, the lifetime of the ion pair R^+X^- is too short ($< 10^{-13}$ s) for it to exist as an intermediate and the substitution reaction of RX is enforced to be concerted. However, the present study shows that the ion pair 1^+Br^- has a significant lifetime and that it is formed in the rate-limiting step. The mechanisms of the elimination and substitution reactions are discussed.



Scheme 2

Results

The solvolysis of 9-(2-bromo-2-propyl)fluorene **1**-Br in acetonitrile provides the alkene 9-isopropenylfluorene **2** as the sole product. Solvolysis in mixtures of water with acetonitrile or methanol yields the substitution products 9-(2-hydroxy-2-propyl)fluorene **1**-OH and 9-(2-methoxy-2-propyl)fluorene **1**-OMe along with alkene **2** (Scheme 2). No trace of 9-isopropylidenefluorene is observed under these conditions. A trace of **1**-NHCOMe is formed in acetonitrile in water. The kinetics of the

Table 1 Rate constants and rate-constant ratios for the reactions of **1**-Br[a] at 25 °C[b]

Solvent[c]	NaX (0.60 mol dm^{-3})	$(k_E + k_S)/10^{-6}$ s^{-1}	$k_E/10^{-6}$ s^{-1}	$k_S/10^{-6}$ s^{-1}	k_E/k_S	k_{MeOH}/k_{HOH}[d]	k_X/k_{HOH}[d]
100% MeCN		3.81	3.81				
		(1.64)	(1.64)				
90% MeCN		39.3	36.3	3.0	12		
70.6% MeCN		237	199	38	5.3		
		(105)	(74)	(31)	(2.4)		
100% MeOH		28.1	23.6	4.5	5.3		
		(12.3)	(8.9)	(3.4)	(2.6)		
90% MeOH		114	93.1	20.9	4.5	0.7	
80% MeOH		315	242	73	3.3	0.6	
70% MeOH		671	481	190	2.5	0.7	
		(291)	(154)	(137)	(1.1)	0.6	
60% MeOH		1860	1256	604	2.1	0.7	
50% MeOH		4170	2530	1640	1.5	0.7	
70% MeOH	$NaClO_4$	937	722	215	3.4	0.7	
	NaOAC	515	398	117	3.4	0.7	
	NaSCN	1060	738	321	2.3	0.6	3
	NaN_3	837	627	210	3.0	0.7	4

[a] Substrate concentration 0.02 mmol dm^{-3}. [b] The values in parentheses refer to reactions of [$^2H_6$]-**1**-Br. [c] By volume in water. [d] Dimensionless ratio of second-order rate constants, *cf.* eqn. (1).

Table 2 Kinetic deuterium isotope effects for the reactions of **1**-Br at 25 °C[a]

Solvent[b]	$(k_E^H + k_S^H)/(k_E^{D6} + k_S^{D6})$	k_E^H/k_E^{D6}	k_S^H/k_S^{D6}
100% MeCN	2.3 ± 0.1	2.3 ± 0.1	
70.6% MeCN	2.3 ± 0.1	2.7 ± 0.1	1.2 ± 0.1
100% MeOH	2.3 ± 0.1	2.7 ± 0.1	1.3 ± 0.1
70% MeOH	2.3 ± 0.1	3.1 ± 0.1	1.4 ± 0.1

[a] The rate constants are recorded in Table 1; the errors are maximum errors (see Experimental). [b] By volume in water.

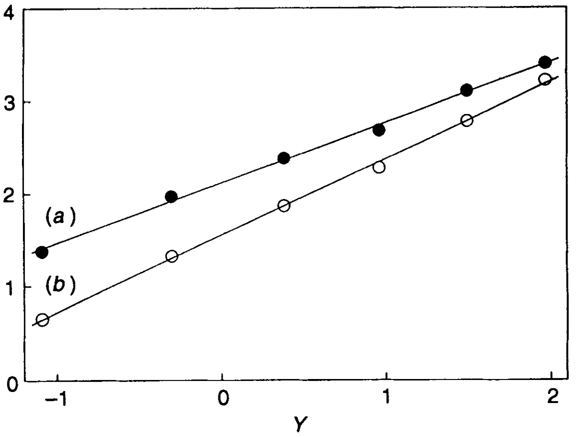


Fig. 1 Grünwald–Winstein plots of the solvolytic elimination (●) and substitution (○) reactions of **1**-Br in methanol–water mixtures. Data from Table 1. The *Y* values are based upon solvolysis of *tert*-butyl chloride.[5] The value for the disappearance of **1**-Br is m_{obs} = 0.70.

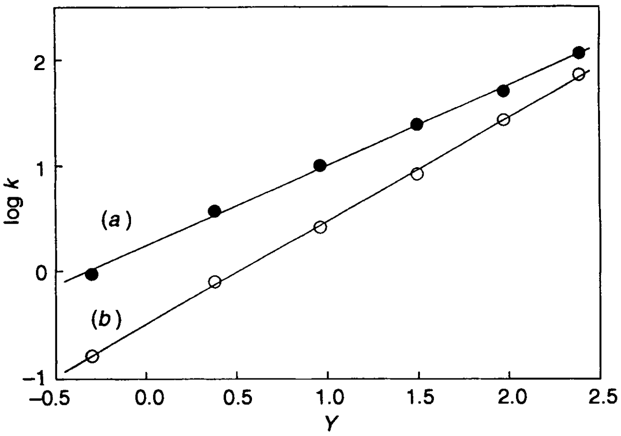


Fig. 2 Grünwald–Winstein plots of the solvolytic elimination (●) and substitution (○) reactions of **1**-Cl in methanol–water mixtures. Data from Table 3. The *Y* values are based upon solvolysis of *tert*-butyl chloride.[5] The value for the disappearance of **1**-Cl is m_{obs} = 0.82.

reactions were studied at 25 °C by a sampling high-performance liquid-chromatography procedure. The measured rate constants and reaction conditions are shown in Table 1.

Addition of salts to the reaction solution has some small effects on the reaction rates and product compositions. Only the most potent nucleophiles give any detectable amount of products. Thus, sodium thiocyanate (0.60 mol dm^{-3}) in 70 vol% methanol in water provides only 2% of **1**-SCN and sodium azide (0.60 mol dm^{-3}) yields 2% of **1**-N_3 (Table 1).

The measured product ratios were used to calculate the discrimination between the reaction of the carbocation intermediate with X^- and water by using eqn. (1). The ratios,

$$k_X/k_{HOH} = ([\mathbf{1}\text{-X}]/[\mathbf{1}\text{-OH}])([H_2O]/[X^-]) \quad (1)$$

which are ratios of second-order rate constants, are given in Table 1.

Relative to **1**-Br, the corresponding deuteriated analogue 9-(2-bromo[$^2H_6$]-2-propyl)fluorene ([$^2H_6$]-**1**-Br) reacts more slowly and gives smaller fractions of the elimination product **2** (Table 1). The measured isotope effects are collected in Table 2.

Grünwald–Winstein plots for the reactions of **1**-Br in methanol–water are shown in Fig. 1. The *Y* values correspond to reaction of *tert*-butyl chloride.[5] Similar plots for **1**-Cl are shown in Fig. 2. These plots are based upon the rate constants for the reaction of **1**-Cl in methanol–water mixtures, which are collected in Table 3. The rate data for **1**-Br in 90 and 70.6 vol% acetonitrile in water (Table 1) and using the *Y* values measured by Bunton and co-workers[6] for the solvolysis of *tert*-butyl chloride in acetonitrile–water yield $m_{obs} \approx 0.74$, $m_E \approx 0.70$ and $m_S \approx 1.05$. Approximate *m*-values based upon rate data for **1**-Cl in 25 and 70.6 vol% acetonitrile in water[1] can be calculated as $m_{obs} \approx 0.84$, $m_E \approx 0.78$ and $m_S \approx 1.09$.

Discussion

The solvolysis of **1**-Br in 70.6 vol% acetonitrile in water is about 100 times faster than the corresponding reaction of **1**-Cl.[1] The ionization of **1**-Br is very sensitive to the ionizing power of the

Table 3 Rate constants and rate-constant ratios for the reactions of **1**-Cl[a] at 25 °C

Solvent[b]	$(k_E + k_S)/10^{-6}\ s^{-1}$	$k_E/10^{-6}\ s^{-1}$	$k_S/10^{-6}\ s^{-1}$	k_E/k_S	k_{MeOH}/k_{HOH}[c]
90% MeOH	1.11	0.94	0.16	5.8	0.6
80% MeOH	4.56	3.76	0.80	4.7	0.6
70% MeOH	12.8	10.1	2.7	3.8	0.6
60% MeOH	32.7	24.3	8.4	2.9	0.6
50% MeOH	83.0	56.2	26.8	2.1	0.6
40% MeOH	188	116	72	1.6	0.6

[a] Substrate concentration 0.02 mmol dm^{-3}. [b] By volume in water. [c] Dimensionless ratio of second-order rate constants, *cf.* eqn. (1).

solvent. The slopes of the Grünwald–Winstein plots, shown in Fig. 1, for reaction in 50 to 100 vol% methanol in water of $m_{obs} = 0.70$, $m_E = 0.65$ and $m_S = 0.83$ are smaller than for a simple carbocation process. A substrate parameter *m* close to unity is expected for a classical S_N1 reaction.[7] Reactions of S_N2 type usually exhibit *m* values in the range 0.25–0.35.[7] However, the value of *m* is not a good mechanistic tool for distinguishing S_N1 and S_N2 reactions since it has been shown that bimolecular substitution reactions can have large values; the reaction of azide ion with substituted 1-phenylethyl chloride exhibited $m = 0.8$.[4] It was explained by a loose, 'exploded', transition state with a large carbocationic character.

The difference in substrate parameter values, m_S is larger than m_E (Fig. 1), shows that the reaction of the ion pair to the alkene has a less polar transition state than the reaction of the ion pair to the substitution product. Accordingly, an increase in solvent polarity increases the fraction of substitution product. The reason is presumably that substitution by the solvent occurs at a more separated stage than elimination. The decrease in ionizing power corresponds to a decrease in the amount of contact ion pairs that go on to solvent-separated ion pairs, which presumably are intermediates on the reaction path from contact ion pair to alcohol and ether. The elimination from the ion pair, as will be discussed below, is expected to occur directly through the contact ion pair, mainly with the leaving group as the hydron-abstracting base. The effect of solvent nucleophilicity on the competition between elimination and substitution from a common carbocationic intermediate should also contribute to the difference in m_E and m_S values.

An increase in the fraction of alkene product with decrease in ionizing power of the solvent has also been observed for the chloride **1**-Cl.[1] This effect has now been quantified by using plots of the Grünwald–Winstein type (Fig. 2). The *m* values are larger for **1**-Cl than for **1**-Br indicating a later rate-limiting ionization transition state for the former. This is in accord with a theoretical study by Hynes and co-workers who found a decreasing activation free energy trend (Cl > Br > I) as well as a decreasing transition-state ionic character for the solvolysis of *tert*-butyl halides.[8]

The competing substitution and elimination reactions of the tertiary cumyl derivative $4\text{-}NO_2C_6H_4C(Me)_2Y$ in 50% trifluoroethanol–water show different sensitivities towards solvent polarity, $m_E = 0.7$ and $m_S = 1.0$.[9] This has been attributed to stepwise substitution through a carbocation intermediate, but the elimination, despite that the substrate is a tertiary one, was concluded to be of a thermal, pericyclic type. This mechanistic interpretation is controversial. It has been pointed out that competing elimination and substitution through a common ion pair is also consistent with the data.[10,11]

The effects of salts on the rate-limiting ionization step are small in 70 vol% methanol in water (Table 1). Small effects of salts were also reported for the reaction of **1**-Cl in 25 vol% acetonitrile in water.[1] No significant rate increase is observed for the strongly nucleophilic thiocyanate or azide ions. However, the formation of substitution products with these nucleophiles is minor, only 2% of **1**-SCN and 2% of **1**-N_3 are formed at a nucleophile concentration of 0.60 mol dm^{-3}. Thus, a significant rate increase is not expected for any parallel bimolecular reaction, *i.e.*, S_N2 reaction or rate-limiting trapping of a reversibly formed carbocation ion-pair intermediate.

The effect of salts (Table 1) on the observed rate constant k_{obs} $(= k_E + k_S)$ could be attributed to specific salt effects on the ionization step. Similar effects have been observed for reaction of **1**-Cl[1] and other solvolysis reactions in aqueous acetonitrile[4,12] as well as in other mixtures of water and organic solvents.[13] Especially large negative salt effects are usually seen for acetate and hydroxide anions.

The measured isotope effects are consistent with competing substitution and elimination reactions *via* a common irreversibly formed ion-pair intermediate [Scheme 3, eqns. (2)–(4), $k_{-1} \ll k_{SOH}$, k_e]. Accordingly, owing to the competition, the measured isotope effects on the substitution reaction and the elimination reaction are attenuated and enlarged, respectively, relative to the isotope effect on the ionization step. This is easily seen by examining the expressions for the isotope effects [eqns. (5)–(8)].

$$k_E = k_1k_e/(k_{-1} + k_{SOH} + k_X[X^-] + k_e) \qquad (2)$$

$$k_S = k_1k_{SOH}/(k_{-1} + k_{SOH} + k_X[X^-] + k_e) \qquad (3)$$

$$k_S + k_E = k_1(k_{SOH} + k_e)/(k_{-1} + k_{SOH} + k_X[X^-] + k_e) \qquad (4)$$

If $k_{-1} \ll k_{SOH}$, k_e and $[X^-] = 0$ the following equations are valid

$$k_E^H/k_E^{D6} = (k_1^H/k_1^{D6})(k_e^H/k_e^{D6})(k_{SOH}^{D6} + k_e^{D6})/(k_{SOH}^H + k_e^H) \qquad (5)$$

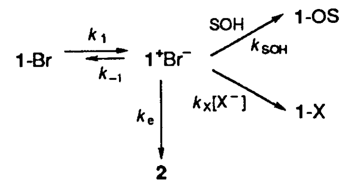
$$k_S^H/k_S^{D6} = (k_1^H/k_1^{D6})(k_{SOH}^H/k_{SOH}^{D6})(k_{SOH}^{D6} + k_e^{D6})/(k_{SOH}^H + k_e^H) \qquad (6)$$

$$(k_S^H + k_E^H)/(k_S^{D6} + k_E^{D6}) = k_1^H/k_1^{D6} \qquad (7)$$

$$\Rightarrow k_E^H/k_E^{D6} > (k_E^H + k_S^H)/(k_E^{D6} + k_S^{D6}) > k_S^H/k_S^{D6} \qquad (8)$$

This has been discussed in some detail for the reactions of the chloride **1**-Cl already and a detailed discussion will not be given here.[1] Competition as the cause of enlarged and attentuated isotope effects have been discussed in several reports and review articles.[10,14]

The isotope effect k_{SOH}^H/k_{SOH}^{D6} should be close to unity. A maximum elimination isotope effect k_E^H/k_E^{D6} is obtained when the fraction of substitution is much larger than elimination, *i.e.*, $k_{SOH} > k_e$ [*cf.* eqn. (5)]. The maximum effect is equal to the secondary β-deuterium isotope effect on the ionization step multiplied by the primary isotope effect on the elimination step.[15] This corresponds to a maximum isotope effect on the substitution reaction [*cf.* eqn. (6)]. When the elimination does



Scheme 3

not compete with substitution, as in pure acetonitrile, the elimination isotope effect is not enlarged but attains the isotope effect of the rate-limiting ionization step (Table 2). The value of the measured isotope effect of $k_{obs}{}^{H}/k_{obs}{}^{D6}$ = 2.3 in this solvent confirms earlier conclusions about irreversible ionization.[1]

The selectivity of the carbocationic intermediate toward different nucleophiles is very small (Table 1). Thus, azide anion and thiocyanate anion are only a few times more reactive than a water molecule toward the intermediate, $k_{N3}/k_{HOH} \approx 4$ and $k_{SCN}/k_{HOH} \approx 3$ (ratios of second-order rate constants) in 70 vol% methanol in water. Also the reactivity of methanol is anomalously low, k_{MeOH}/k_{HOH} = 0.6–0.7 (Table 1).[16] Methanol is usually more reactive than water due to its higher nucleophilicity. For example, values of k_{MeOH}/k_{HOH} of 6.4 and 2.1, respectively, have been reported for the carbocations $Ph_2C(Me)^+$ and p-$MeC_6H_4CH_2{}^+$.[12,17] However, the selectivity values are close to those measured for **1**-Cl, $k_{N3}/k_{HOH} \approx 5$ (in 25 vol% MeCN in water) and $k_{MeOH}/k_{HOH} \approx 0.6$.[1]

The observed low selectivity suggests that the intermediate has a very short lifetime. Assuming a diffusion-controlled reaction with azide and thiocyanate ions, with a rate constant of $k_d = 5 \times 10^9$ dm^3 mol^{-1} s^{-1}, makes it possible to estimate the rate constants k_e and k_{SOH} (Scheme 3). Thus, the rate constants for reaction of the intermediate to elimination and substitution products in 70 vol% methanol are $k_e \approx 1 \times 10^{11}$ s^{-1} and $k_{SOH} = k_{MeOH} + k_{HOH} \approx 4 \times 10^{10}$ s^{-1}. These large constants indicate that the intermediate is very short-lived and that the products are formed mainly by a direct route from the ion pair and not after a prior diffusional separation (k_{-d}) of the ion pair. The rate constant of diffusional separation can be estimated as $k_{-d} \approx 2 \times 10^{10}$ s^{-1} assuming an association constant (K_{as}) for the ion-pair formation of K_{as} = 0.2–0.3 dm^3 mol^{-1}.[1,18]

The reactivity of the ion pair is so high that the reactions presumably occur within a pool of solvent molecules and added reactants that are present when the carbocationic intermediate is born.[1,19] The rotational correlation time of water, which has been estimated as $\tau \approx 10^{-11}$ s,[20] may be used as a rough estimate of the time required for the reorientation of a solvent molecule. Faster processes occur by preassociation mechanisms in which the reactant, a water or a methanol molecule, is in reaction position before the intermediate is formed.

It has been pointed out recently that the 'azide-clock' method may have a limited value in estimating the lifetime of a very short-lived carbocationic intermediate formed by solvolysis.[17] Thus, recent results suggest that the leaving group of the ion pair influences the reactivity and selectivity of short-lived carbocations.[17] Therefore, the reactivity estimated for the ion pair 1^+Br^- is crude; it is not expected to be similar to the reactivity of the free carbocation.

Theoretical as well as experimental results by Carpenter and co-workers indicate that competing reactions can occur through a common transition state with no barrier for formation of the products.[21] The 'flow direction' through the saddle point determines the product ratio. However, the results for **1**-Br show that there are barriers to hydron abstraction and to substitution of the ion-pair intermediate.

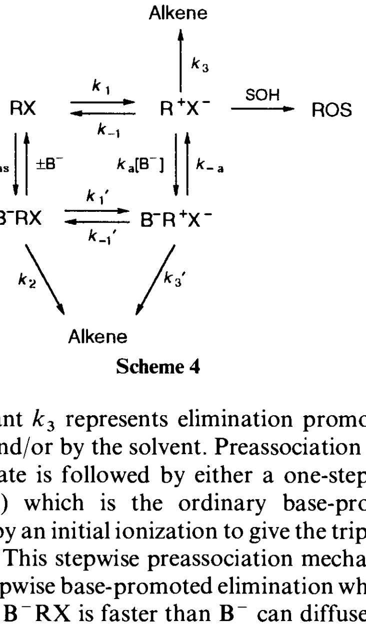
A trace of the amide **1**-NHCOMe is formed in solvents having a large fraction of acetonitrile. This product is expected to be formed by nucleophilic attack by MeCN on the ion pair to give the nitrilium ion **1**-N≡CMe$^+$. Subsequent hydrolysis by water provides the amide.[22] The alkene is the exclusive product in 100% acetonitrile.

Classical E1 reactions, defined as elimination exclusively from a free carbocation, are presumably not common for solvolytic reactions of substrates with leaving groups which are negatively charged or are neutral but efficient bases.[10] Thus, it has been found that the leaving group of an ion pair is often very efficient in promoting elimination by abstraction of a β-hydron, even for substrates which form relatively stable carbocations in highly aqueous media.[10,12] The high efficiency of the leaving group as a hydron acceptor is most likely caused by a proximity effect as well as by its high basicity, owing to incomplete solvation.

The reaction of **1**-Br is expected to give the alkene almost exclusively from the ion pair. Much of the elimination should arise from hydron-abstraction by the leaving group Br$^-$. The basicity of Br$^-$ is low, $pK_{HBr} = -9$ in water, compared with $pK_{HCl} = -6$.[23] Consistently, the fraction of elimination is smaller for **1**-Br than for **1**-Cl.[1]

Addition of acetate ion has been found to increase the elimination-to-substitution ratio in 25 vol% acetonitrile in water.[1] This result indicates that the elimination from the ion pair is catalysed by general bases. The Brønsted parameter for **1**-Br as well as for **1**-Cl was measured as $\beta = 0.05$ with substituted acetate anions.[1] Consistently, a very small isotope effect of $k_e{}^{H}/k_e{}^{D6}$ *ca.* 2.8 has been estimated for **1**-Cl.[1] Also, catalysis from halide ions, Cl$^-$ and Br$^-$, is described rather well with the same Brønsted line. A similar value, which indicates a very small amount of hydron transfer in the elimination transition state, is expected for **1**-Br in 70 vol% methanol in water, but since catalysis is less important in this solvent, it was not possible to measure the Brønsted parameter. The reason for the insignificant amount of catalysis is not known.

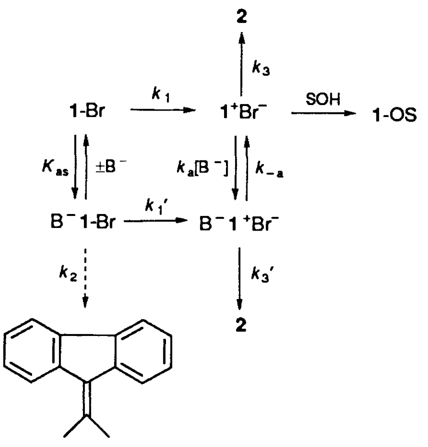
Scheme 4 shows various reaction paths of alkene formation.



Scheme 4

The rate constant k_3 represents elimination promoted by the leaving group and/or by the solvent. Preassociation of the base with the substrate is followed by either a one-step concerted elimination (k_2) which is the ordinary base-promoted E2 mechanism, or by an initial ionization to give the triple ion complex $B^-R^+X^-$. This stepwise preassociation mechanism[3,10] is preferred for stepwise base-promoted elimination when collapse of $B^-R^+X^-$ to B^-RX is faster than B^- can diffuse away, *i.e.*, $k_{-1}' > k_{-a}$.

It has usually been assumed that collapse (k_{-1}) is much faster than diffusional separation (k_{-a}) when X^- is a potent nucleophile.[24] However, it was recently pointed out that major reorganization of carbocation structure and solvent might lead to slow collapse.[10] This seems to be the reason why internal return is slow for **1**-Br. Accordingly, the mechanistic scheme for the bromide can be reduced to Scheme 5. This scheme also includes the E2 reaction of **1**-Br which requires a strong base (see below). The alkene product formed by



Scheme 5

this route (k_2) is not the same as the product formed by the k_3 and k_3' processes.

Apparently, the methyl hydrons of the ion pair $\mathbf{1}^+Br^-$ are kinetically much more acidic than the 9-hydron since the thermodynamically much more stable alkene 9-isopropylidenefluorene is not formed.[25] However, this product is formed by E2 reaction with strong base.[1,26] The isotope effect on this E2 reaction with **1**-Cl, using substrate deuteriated in the 9-position, has been measured as $k^H/k^D = 8.1$.[26] Also in other elimination reactions, strong base has been found to favour the E2 reaction by abstracting the more acidic hydron.[27] Weak base, on the other hand, favours a stepwise solvolytic reaction which often involves abstraction of the less acidic hydron.

The reason for the exclusive formation of alkene **2** from the solvolysis of **1**-Br should be the large hyperconjugative stabilization of the carbocation which is indicated by the large ionization isotope effect of $k_{obs}{}^H/k_{obs}{}^{D6} = 2.3$ (equal to 1.15/β-D). Values of 1.10 ± 0.05/β-D have been reported for secondary isotope effects.[28] The large value of 2.3 shows that the bonds to the methyl hydrons are already weakened considerably in the ionization step. This should have the effect of increasing the kinetic acidity of the methyl hydrons. The deuterium isotope effect for the solvolysis of 9-(2-chloro-2-propyl)[9-^{2}H]fluorene was measured as $(k_{12}{}^H + k_{13}{}^H)/(k_{12}{}^D + k_{13}{}^D) = 1.03$.[1]

In summary, the reason for the significant lifetime of the bromide ion pair is concluded to be a considerable reorganization of the carbocation structure (and this is presumably coupled with a substantial solvent reorganization) which accompanies the ionization of **1**-Br. These processes slow down the collapse of the ion pair back to covalent material. The measured isotope effects support this conclusion about slow internal return.

Experimental

General.—The ^{1}H NMR analyses were performed with a Varian XL 300 spectrometer. The high performance liquid chromatography (HPLC) analyses were carried out with a Hewlett-Packard 1090 liquid chromatograph equipped with a diode-array detector on a C8 or a C18 (5 μm, 3 × 100 mm) reversed phase column. The mobile phase was a solution of methanol or acetonitrile in water. The reactions were studied at constant temperature in a HETO 01 PT 623 thermostat bath. The semi-preparative HPLC separations were carried out with a Hewlett-Packard 1084B HPLC apparatus using a semi-preparative C8 column (7 μm, 8 × 250 mm) using methanol–water as mobile phase.

Materials.—Acetonitrile (Riedel de Haen) and methanol (J. T. Baker or Merck) were of HPLC grade and were used without further purification. The syntheses of 9-(2-bromo-2-propyl)fluorene **1**-Br and 9-(2-chloro-2-propyl)fluorene **1**-Cl have been described previously.[1] The deuteriated substrate ([$^2H_6$]-**1**-Br) was prepared from the corresponding deuteriated alcohol [$^2H_6$]-**1**-OH, having >99.0 atom% ^{2}H in the methyl groups, according to the same method.

Kinetics and Product Studies.—The reaction solutions were prepared by mixing acetonitrile or methanol with the cosolvent at room temp., *ca.* 22 °C. The reaction flask was a 2 cm^3 HPLC flask, sealed with a gas-tight PTFE septum, which was placed in an aluminium block in the water thermostat bath. The reactions were initiated by fast addition of a few microlitres, by means of a syringe, of the substrate dissolved in acetonitrile. The concentration of the substrate in the reaction solution was usually about 0.02 mmol dm^{-3}. At appropriate intervals, samples were analysed on the HPLC apparatus. The rate constants for the disappearance of the substrates were calculated from plots of area of substrate peak *versus* time by means of a non-linear least-squares regression computer program. Very good pseudo-first-order behaviour was seen for all of the reactions studied. The separate rate constants for the elimination and substitution reactions were calculated by combination of the product composition data, obtained from the peak areas and the relative response factors determined in separate experiments, with the observed rate constants.

The estimated errors are considered as maximum errors derived from maximum systematic errors and random errors.

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