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**Supplementary Material Available:** Tables of chemical shift data as a function of sulfuric acid percent by weight (5 pages). Ordering information is given on any current masthead page.

# Borderline between E1cB and E2 Mechanisms. Elimination of HCl from Fluorene Derivatives

**Alf Thibblin**

*Contribution from the Institute of Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden.* *Received September 2, 1987. Revised Manuscript Received February 17, 1988*

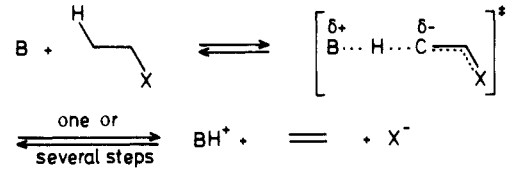
**Abstract:** The base-promoted elimination of HCl from 9-(2-chloro-2-propyl)fluorene (**2**-Cl) exhibits a kinetic deuterium isotope effect that varies with base strength and solvent character, from a maximum of $k^H/k^D = 8.1$ with $HO^-$ in 25 vol % acetonitrile in water to ~3 in pyridine (neat) at 25 °C. The Brønsted parameter was measured in methanol with substituted quinuclidine bases as $\beta = 0.5$. The large variation in isotope effect could be the result of a varying degree of internal return from a tightly hydrogen-bonded carbanion. However, analysis of $\beta$ as a function of substrate acidity, leaving group, and $\alpha$-substituents suggests that the elimination of HCl from the fluorene derivatives is of E2 type. For example, a change in leaving group from $AcO^-$ to $Cl^-$ corresponds to a decrease in $\beta$ from 0.73 to 0.56 for the 9-(X-methyl)fluorene (**3**-X) series. It is concluded that the reaction coordinate has a relatively large horizontal component corresponding to proton transfer.

There has for a long time been controversy about the position of the mechanistic borderline between stepwise elimination reactions proceeding via a carbanionic intermediate (E1cB) and concerted one-step reactions (E2). What is the dependence of mechanism on structure? For example, is a stepwise mechanism possible for efficient leaving groups? Is there a switch of mechanism on crossing the borderline, i.e., do the mechanisms merge at the borderline, or are both reaction paths employed simultaneously?

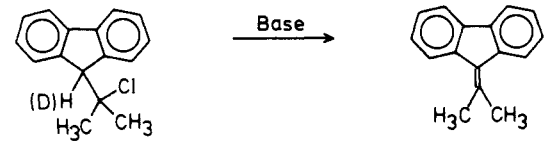
Attempts have been made to distinguish between E2 and irreversible E1cB reactions ($E1cB_I$) by comparing elimination rates with estimated ionization rates,[1-8] derived, for example, from linear free-energy relationships of Taft type.[4,6] A positive deviation from such a plot has been considered as an indication in favor of the E2 mechanism. This is in accord with the traditional view that E1cB reactions do not involve significant weakening of the bond to the leaving group in the initial proton-abstracting step.[9] Only "inductive" interaction between the leaving group and the carbanionic reaction center is assumed.

We have expressed a different view,[10-13] Thus, the substituent and leaving-group effects are discussed in terms of varying degree of cleavage of the bond to the leaving group in the transition state.

**Scheme I**

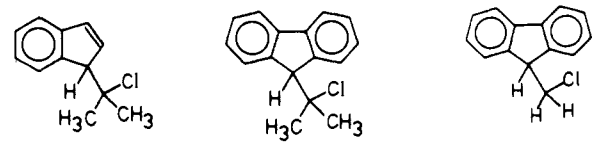


**Scheme II**



*2-Cl* *4*

This assistance to proton removal from the electron-withdrawing group X (potential leaving group) results in a unifying view of E2 and E1cB reactions. The hyperconjugative interaction is largest when the base is in a periplanar position relative to the leaving group (Scheme I). The leaving-group ability of X is quantitatively accounted for by a new type of free-energy relationship.[13]



*1-Cl* *2-Cl* *3-Cl*

Strong evidence has been presented that the elimination of HCl from **1**-Cl in methanol is a stepwise reaction; the intermediate is a carbanion hydrogen bonded to the conjugate acid of the proton-abstracting base,[11,14,15] It has been concluded that the

(1) Hine, J.; Ramsay, O. B. *J. Am. Chem. Soc.* **1962**, *84*, 973-976.
(2) Bordwell, F. G. *Acc. Chem. Res.* **1970**, *3*, 281-290; **1972**, *5*, 374-381.
(3) Cann, P. F.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, *2*, 820-823.
(4) More O'Ferrall, R. A.; Warren, P. J. *J. Chem. Soc., Chem. Commun.* **1975**, 483-484.
(5) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19-25.
(6) More O'Ferrall, R. A.; Warren, P. J.; Ward, P. M. *Acta Univ. Ups., Symp. Univ. Ups.* **1978**, *12*, 209-218.
(7) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1914-1919.
(8) Cavestri, R. C.; Fedor, L. R. J. *J. Am. Chem. Soc.* **1970**, *92*, 4610-4613. Fedor, L. R.; Glave, W. R. *J. Am. Chem. Soc.* **1971**, *93*, 985-989.
(9) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley-Interscience: New York, 1973.
(10) Ahlberg, P. *Chem. Scr.* **1973**, *3*, 183-189.
(11) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1977**, *99*, 7926-7930.
(12) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1979**, *101*, 7311-7317.
(13) Thibblin, A. *Chem. Scr.* **1980**, *15*, 121-127.
(14) Ölwegård, M.; McEwen, I.; Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1985**, *107*, 7494-7499.

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**Table I.** Rate Constants and Isotope Effects for the Base-Promoted Reaction of **2**-Cl Yielding **4** at 25.00 ± 0.03 °C

| solvent | base | $10^6k^{H,a}$ $M^{-1}$ $s^{-1}$ | $10^6k^{D,a}$ $M^{-1}$ $s^{-1}$ | $k^H/k^D$ |
|---|---|---|---|---|
| $H_2O$/ $CH_3CN$[b] | NaOH | 1950[c] | 241[c] | 8.1 ± 1.0[c] |
| MeOH | none | ~0.003 | | |
| MeOH | NaOMe[d] | 1513 | 230 | 6.6 ± 0.5 |
| MeOH | quinuclidine (Q)[e] | 270 | 49.2 | 5.5 ± 0.4 |
| MeOH | diazabicyclooctane (DABCO)[f] | 49.9 | 10.9 | 4.6 ± 0.2 |
| MeOH | diazabicyclooctane (DABCO)[f] | 581[g] | 147[g] | 4.0 ± 0.2[g] |
| MeOH | hexamethylene-tetramine (HMTA)[h] | 1.05 | 0.229 | 4.6 ± 0.3 |
| *t*-BuOH | quinuclidine (Q)[i] | 530 | 104 | 5.1 ± 0.4 |
| *t*-BuOH | diazabicyclooctane (DABCO)[f] | 140 | 32.1 | 4.3 ± 0.2 |
| pyridine | pyridine (P) | ~0.6[j] | ~0.2[j] | ~3.0 |
| pyridine | pyridine (P) | 177[j,k] | 62.0[j,k] | 2.9 ± 0.2[k] |

[a] Estimated maximum error <5% if not otherwise stated. [b] 25 Vol % $CH_3CN$. [c] Reference 24. [d] 0.1 M. [e] 0.45 M, buffered with 5% of base $H^+$. [f] 1 M, buffered with 3% of base $H^+$. [g] 50 °C. [h] 0.42 M, buffered with 2% of base $H^+$. [i] 0.43 M, buffered with 3% of base $H^+$. [j] First-order rate constant ($s^{-1}$). [k] 85 °C.

reaction of **1**-Cl, as well as of the corresponding substrates (**1**-X) with less efficient leaving groups $X^-$, involves a varying degree of internal return.[11-22] Medium and base strength as well as the nature of X affect the amount of internal return.

It has been suggested that the fluorene derivative **2**-Cl, which should be about 2 $pK_a$ units less acidic than **1**-Cl,[23] reacts with methoxide anion in methanol by an E2 mechanism.[4,6] If this is not correct, i.e., the reaction is stepwise instead, it should exhibit an equal or greater amount of internal return than **1**-Cl under the same reaction conditions. The present work was started with the intention of searching for internal return in the reaction of **2**-Cl with different types of bases and solvents.

## Results

The reaction of 9-(2-chloro-2-propyl)fluorene (**2**-Cl) with bases provides 9-isopropylidenefluorene (**4**) (Scheme II). At low base concentration and/or with bases with low basicity, **4** is accompanied by the solvolysis product 9-(2-propenyl)fluorene (**5**) and, in methanol, 9-(2-methoxy-2-propyl)fluorene (**2**-OMe). A significant amount of solvolysis was only observed in the slow kinetic runs with hexamethylenetetramine (HMTA), Control experiments showed the rearrangement of **5** to **4** to be very slow under the reaction conditions. Accordingly, no correction for this process was necessary with the amines. The rate constants obtained for the reaction of **2**-Cl and its deuteriated analogue with pyridine at 25 °C were found to increase with reaction time. Only approximate rate constants are therefore recorded in Table I.

The kinetics of the reactions were studied by a sampling high-performance liquid chromatography procedure. The measured rate constants and reaction conditions are shown in Table I, which also includes the reaction of the deuteriated analogue (9-$^2$H)-9-(2-chloro-2-propyl)fluorene (*d*-**2**-Cl).

Table II summarizes old and new data with 1-(2-chloro-2-propyl)indene (**1**-Cl), 1-(2-bromo-2-propyl)indene (**1**-Br), 1-(2-acetoxy-2-propyl)indene (**1**-OAc), 9-(chloromethyl)fluorene (**3**-Cl), and 9-(acetoxymethyl)fluorene (**3**-OAc) in methanol. The isotope effect for the reaction of **1**-Cl with pyridine has approximately the same value in methanol and pyridine.

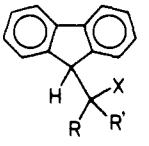
**Table II.** Rate Constants and Isotope Effects for the Reactions of **1**-Cl, **3**-Cl, and **3**-OAc in Methanol at 25.00 ± 0.03 °C

| substrate | base | $10^6k^{H,a}$ $M^{-1}$ $s^{-1}$ | $k^H/k^D$ |
|---|---|---|---|
| **1**-Br | quinuclidine (Q)[b] | 143000 | |
| **1**-Br | diazabicyclooctane (DABCO)[c] | 28400 | |
| **1**-Cl | quinuclidine (Q)[d] | 36000[e] | 7.9[f] |
| **1**-Cl | diazabicyclooctane (DABCO)[g] | 6190 | |
| **1**-Cl | pyridine (P)[h] | 8.0[i] | 5.6[i] |
| **1**-Cl | pyridine (P) (neat) | 460[j] | 5.5 ± 0.4 |
| **3**-Cl | quinuclidine (Q)[d] | 42500[e] | |
| **3**-Cl | diazabicyclooctane (DABCO)[g] | 4600 | |
| **3**-OAc | quinuclidine (Q)[d] | 892 | |
| **3**-OAc | diazabicyclooctane (DABCO)[h] | 40.5 | |

[a] Estimated maximum error <5% if not otherwise stated. [b] 18 mM, buffered with 5% of base $H^+$. [c] 60 mM, buffered with 3% of base $H^+$. [d] 0.12 M, buffered with 5% of base $H^+$. [e] Reference 25. [f] With ethylpiperidine at 30 °C, ref 14. [g] 0.1 M, buffered with 3% of base $H^+$. [h] 1 M, buffered with 3% of base $H^+$. [i] At 30 °C, ref 14. [j] First-order rate constant ($s^{-1}$).

## Discussion

Base-promoted elimination reactions with fluorene derivatives have been studied in great detail by More O'Ferrall and coworkers.[4,6,26-30] They concluded that the methoxide-promoted elimination in methanol from compounds of the following type with leaving group X = Cl or Br is of E2 type.[4,6] With less efficient leaving groups, such as carboxylate anions or tertiary amines, the




R,R' = H,$CH_3$

elimination was concluded to be E1cB$_1$.[28-30] The assignment of the E2 mechanism for the chloro and bromo compounds was based upon the observation of elimination rates that were larger than estimated ionization rates.

We have questioned the conclusion that the fluorene derivatives with chloride anion as leaving group react by the E2 mechanism. A hyperconjugative stabilization of the ionization transition state by the Cl substituent may account for the positive deviation in reaction rate.

Our scepticism is grounded on results obtained with the structurally closely related indene substrates. These results provide strong evidence that **1**-Cl reacts stepwise in methanol with tertiary amines as well as with methoxide anion.[11,14,15] Thus, the elimination of HX and the competing base-catalyzed 1,3-proton transfer of **1**-X have been found to be coupled via a common hydrogen-bonded carbanion. The total reaction of **1**-X (elimination plus 1,3-proton transfer) was found to increase with increased polarity of the substituent X and with increased ability of X to stabilize the transition state by hyperconjugation, However, increased leaving-group ability of X decreases the rearrangement rate drastically, which constitutes a strong indication for a coupled mechanism via a common carbanion intermediate.[11] Another piece of independent evidence in favor of a stepwise elimination mechanism is provided by the enlarged kinetic deuterium isotope effects measured for the competing base-catalyzed 1,3-hydron

(15) Ahlberg, P.; Thibblin, A. *Synthesis and Applications of Isotopically Labeled Compounds 1985*; Proceedings of the Second International Symposium, Kansas City, MO; Elsevier Science Publishers BV.: Amsterdam, 1986; pp 89-94.
(16) Thibblin, A.; Ahlberg, P. *Acta Chem. Scand.* **1974**, *B28*, 818-820.
(17) Thibblin, A.; Ahlberg, P. *Acta Chem. Scand.* **1976**, *B30*, 555-561.
(18) Thibblin, A.; Bengtsson, S.; Ahlberg, P. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1569-1576.
(19) Thibblin, A.; Onyido, I.; Ahlberg, P. *Chem. Scr.* **1982**, *19*, 145-149.
(20) Thibblin, A. *Chem. Scr.* **1983**, *22*, 182-187.
(21) Thibblin, A. *J. Am. Chem. Soc.* **1983**, *105*, 853-858.
(22) Thibblin, A. *J. Chem. Soc., Chem. Commun.* **1984**, 92-93.
(23) Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963-968.
(24) Thibblin, A. *J. Am. Chem. Soc.* **1987**, *109*, 2071-2076.
(25) Thibblin, A. *J. Am. Chem. Soc.* **1984**, *106*, 183-186.
(26) More O'Ferrall, R. A.; Slae, S. *J. Chem. Soc. B* **1970**, 260-268.
(27) More O'Ferrall, R. A.; Warren, P. J. *Proc. R.I.A.* **1977**, *77B*, 513-521.
(28) Kelly, R. P.; More O'Ferrall, R. A.; O'Brien, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 211-219.
(29) More O'Ferrall, R. A.; Larkin, F.; Walsh, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1573-1579.
(30) Larkin, F.; More O'Ferrall, R. A. *Aust. J. Chem.* **1983**, *36*, 1831-1842.

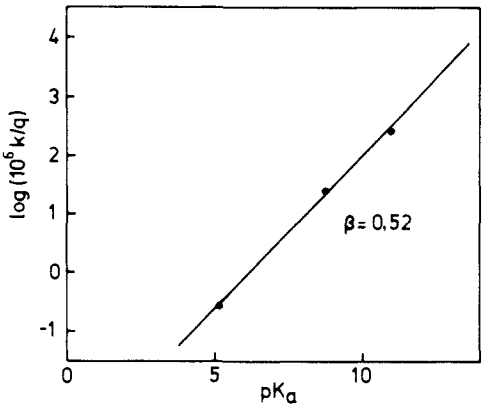



**Figure 1.** Brønsted plot for the reaction of **2**-Cl with tertiary amines in methanol at 25 °C.

transfer reaction of **1**-OAc[11,18,20,21,31,32] and of **1**-Cl,[14,15]

**Search for Internal Return.** An indirect way of obtaining evidence for a carbanion intermediate in the reaction of **2**-Cl is to detect internal return. Potential methods for doing this are (i) studies of kinetic deuterium isotope effect as a function of the basicity of the proton-abstracting base, (ii) rate-constant measurements for bases of different base strength (a curved Brønsted plot is consistent with a large amount of internal return), (iii) anomalous temperature effects on the kinetic isotope effect,[19,33,34] and (iv) deviation from the Swain–Schaad relation,[35] $k^H/k^D = (k^D/k^T)^{2.344}$.

Fluorene is about 2–3 p$K_a$ units[23] less acidic than indene and its conjugate base is therefore more easily reprotonated. Accordingly, a hypothetical carbanionic intermediate formed from **2**-Cl is expected to undergo internal return more easily than the corresponding intermediate of the indene derivative. Consistently, the kinetic isotope effects with the amines are lower for **2**-Cl than for **1**-Cl (Tables I and II). The measured interval in isotope effect of ~3–8.1 may be explained alternatively by an E2 mechanism involving a varying degree of proton transfer. However, such a large change in isotope effect for such a relatively small change in reaction conditions is usually not observed for E2 reactions. McLennan and co-workers have assigned the E1cB$_1$ mechanism to the reaction of $(p\text{-}ClC_6H_4)_2CHCCl_3$, which exhibits a span in isotope effect of $k^H/k^D$ = 3.1–6.2 in ethanol at 45 °C for a variation in base strength of 7 p$K_a$ units;[36] the p$K_a$ of the substrate was estimated at ca. 26.[37]

The Brønsted plot of Figure 1 is not significantly curved. A rather large change in the amount of internal return is required to detect a significant deviation from linearity of the Brønsted plot. Nevertheless, a significant amount of internal return may be "hidden" in the rate constants, resulting in too large a $\beta$ value. However, correction for possible internal return may, at most, decrease the measured $\beta$ parameter by 0.01 unit.

A temperature effect study on the observed isotope effect is another potential method for obtaining indications for a stepwise mechanism. Accordingly, under certain circumstances, a simple stepwise mechanism may result in an anomalous temperature effect on the measured isotope effect.[38] For example, if $k_{-1}$ and $k_2$ of eq 1 show different sensitivity to isotopic substitution and the Arrhenius preexponential factors are quite different, the result

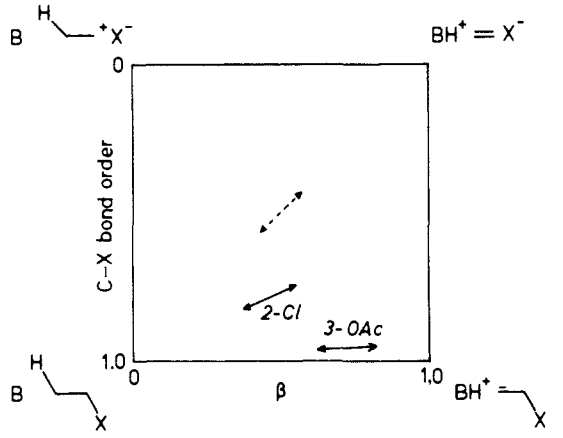



**Figure 2.** Reaction coordinate energy diagram for base-promoted $\beta$-elimination reactions; the energy contour lines are omitted. A "central, diagonal" transition state is indicated, and suggested transition-state positions and reaction coordinate directions for the concerted elimination of HCl from **2**-Cl and the stepwise elimination of HOAc from **3**-OAc with tertiary amines in methanol are shown.

may be a constant, or even decreasing, kinetic isotope effect on $k_{obsd}$ with temperature. However, on the other hand, a normal temperature effect on the isotope effect does not rule out a stepwise mechanism. A simple simulation of $k_{obsd}{}^H/k_{obsd}{}^D$ with temperature based upon eq 1 shows that a large amount of internal return yields anomalous temperature effects for a large range of Arrhenius preexponential factor ratio $A_2/A_{-1}$.[34]

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} B \qquad (1)$$

Experimentally, anomalous temperature effects have been found for base-promoted elimination reactions, e.g., the elimination of HCl from $C_6H_5CHClCF_2Cl$ in NaOEt/EtOH[39] and the elimination of HOAc from 3-(2-acetoxy-2-propyl)indene in methanol or acetonitrile/water with tertiary amines.[19] Independent conclusive evidence shows that the latter reaction is a stepwise 1,4-elimination reaction,[11-22]

The temperature effect on $k^H/k^D$ for the elimination with DABCO in methanol (Table I) is normal, i.e., is in accord with the Arrhenius equation for a one-step reaction. However, as discussed above, this does not disqualify the E1cB mechanism. The data with pyridine are unfortunately not sufficiently precise to allow the conclusion that there is an anomalous temperature effect on the isotope effect.

**Degree of Proton Transfer Relative to Reactant Structure.** Reaction-coordinate energy diagrams of the type shown in Figure 2 are convenient for mapping the characteristics of the transition state of $\beta$-elimination reactions. Diagrams of this type are often referred to as More O'Ferrall–Jencks diagrams.[40-44] The $x$ and $y$ axes can be defined by bond order or by the experimental Brønsted parameters $\beta$ for proton transfer and $\beta_{lg}$ for breaking of the bond to the leaving group. The $z$ axis, perpendicular to the $x$–$y$ plane, corresponds to energy. It is often indicated by contour lines. The change in the position of the transition state resulting from a change in structure of one of the reactants can be predicted and visualized conveniently by this type of diagram.

For example, the introduction of $\alpha$-methyl substituents in the substrate is expected to stabilize both the carbocationic intermediate (upper-left corner of Figure 2) and the products (upper-right corner), resulting in a lowering of the top edge of the

(31) Ahlberg, P. *Chem. Scr.* **1973**, *4*, 33–39.
(32) Bengtsson, S.; Ahlberg, P. *Chem. Scr.* **1974**, *6*, 45–46.
(33) Koch, H. F.; Dahlberg, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6102–6107.
(34) Thibblin, A. *J. Phys. Org. Chem.*, in press.
(35) (a) Swain, C. G.; Stivers, E. C.; Reuwer, J. F., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1958**, *80*, 5885–5893. (b) Streitwieser, A., Jr.; Hollyhead, W. B.; Sonnichsen, G.; Pudjaatmaka, A. H.; Chang, C. J.; Kruger, T. L. *J. Am. Chem. Soc.* **1971**, *93*, 5096–5102.
(36) McLennan, D. J.; Wong, R. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 526–532.
(37) McLennan, D. J.; Wong, R. J. *Aust. J. Chem.* **1976**, 787–798.
(38) This is a much more sensitive probe of a stepwise mechanism than curvature of Arrhenius plots.[19,34]
(39) Koch, H. F.; Dahlberg, D. B.; McEntee, M. F.; Klecha, C. J. *J. Am. Chem. Soc.* **1976**, *98*, 1060–1061.
(40) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274–277.
(41) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705–718.
(42) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948–7960.
(43) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937–1951.
(44) Winey, D. A.; Thornton, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 3102–3108.

**Table III.** Measured $\beta$ Values for the Base-Promoted Elimination Reactions of **1**-X, **2**-X, and **3**-X with Tertiary Amines in Methanol at 25 °C and the Suggested Changes in Mechanism

| | | | | |
|---|---|---|---|---|
| | | (1) $\alpha$-Substitution | | |
| **3**-Cl | | **2**-Cl | | |
| 0.56 | → | 0.46 | ⇒ | both E2 reactions (or change in mechanism from E1cB to E2) |
| | | (2) Better Leaving Group | | |
| **1**-OAc[a] | | **1**-Cl | | |
| 0.48 | → | 0.47 | ⇒ | both E1cB reactions[b] |
| **1**-Br | | | | |
| 0.45 | | | | |
| **3**-OAc | | **3**-Cl | | |
| 0.73 | → | 0.56 | ⇒ | both E2 or change in mechanism from E1cB to E2 |
| | | (3) More Acidic Substrate | | |
| **2**-Cl | | **1**-Cl | | |
| 0.46 | → | 0.47 | ⇒ | change in mechanism from E2 to E1cB[b] |

[a] At 30 °C;[18] not corrected for internal return. [b] The reaction of **1**-Cl is of E1cB type.[11,14,15]

diagram. This implies a decrease in $\beta$ for a transition state on a reaction coordinate that has a more or less diagonal character, i.e., an E2 transition state. On the other hand, the methyl substituents are predicted to have a slight destabilizing effect on a plausible carbanionic intermediate that corresponds to a small increase in $\beta$ for an E1cB reaction.

Change of leaving group to a more efficient one is also expected to lower the top edge of the diagram and, accordingly, results in a decrease in $\beta$ for an E2 reaction. The position of the E1cB transition state is not significantly shifted by this change in leaving group.

The effect of increasing acidity of the substrate is a lowering of the energy of the carbanionic intermediate in the lower right-hand corner of the diagram. This corresponds to an increase in $\beta$ if the transition state of the E2 reaction is on a reaction coordinate that has a relatively large vertical component. Conversely, a large horizontal component, corresponding to proton transfer, yields a decrease in $\beta$ for the E2 reaction as well as for the E1cB reaction.

A stronger base results in a lowering of the right side of the diagram that shifts the transition state on a diagonal reaction coordinate downward but causes relatively little movement laterally, i.e., only a small change in $\beta$ is expected. However, if the reaction coordinate is horizontal at the transition state, as it is for an E1cB reaction, a shift of the transition state toward the reactants, corresponding to less proton transfer and a decrease in $\beta$, is expected.

Table III summarizes the $\beta$ parameters measured with DABCO and quinuclidine in methanol, and the changes in mechanism that are in accord with the observed changes in $\beta$ values. Different sets of catalysts often yield slightly different Brønsted parameters. The employment of the same set of bases and solvent minimizes the problem with systematic errors of this type. The value of $\beta$ = 0.73 for the reaction of **3**-OAc is of the same magnitude as the value that can be calculated from the solvent isotope effect for the E1cB reaction of **3**-OMe with $MeO^-$, $k_{MeOD}/k_{MeOH}$ = 2.1;[27] the relation $2.63^{\beta} = 2.1$[44,45] yields $\beta$ = 0.77. The significant decrease in $\beta$ for a change in leaving group (corresponding to a positive $p_{xy}$ coefficient)[43] from $AcO^-$ (0.73) to $Cl^-$ for **3**-X (0.56) (entry 2 in Table III) suggests that the reaction of the chloride is of E2 type. Moreover, the very similar $\beta$ values for **1**-Cl and **2**-Cl (entry 3 in Table III) suggest that the elimination from **2**-Cl is an E2 reaction. The decrease occurring in $\beta$ from 0.56 to 0.46 when the $\alpha$ substituents are introduced in the chloride (entry 1 in Table III) is also consistent with the conclusion that the reactions of these two fluorene chlorides are of E2 type.

The decrease in $\beta$ from 0.47 to 0.45 for the indene series for change in leaving group from $Cl^-$ to $Br^-$ is consist with a shift to an E2 mechanism for the bromo compound. However, owing to the experimental error in $\beta$ as well as the uncertainty of making mechanistic conclusions based upon such small differences, the change is certainly too small to constitute any conclusive evidence for such a shift in mechanism. The reactivity ratio $k_{Br}/k_{Cl}$ is ten with methoxide anion and about five with tertiary amines.[11,13] Accordingly, provided that the E1cB and the E2 transition-state structures are not quite similar, a mechanistic shift may be consistent with Rappoport's suggestion that Br and Cl have very similar hyperconjugative stabilizing effects on a carbanion as well as on the rate-limiting transition state for the formation of a carbanionic intermediate.[45]

The large variation in kinetic deuterium isotope effect for **2**-Cl with base strength and solvent could, as discussed above, be the result of some internal return. However, in view of the indications in favor of the E2 mechanism presented in Table III an alternative explanation has to be found. Accordingly, the reaction coordinate is expected to have a large horizontal component at the saddle point ($p_{xy}' \sim 0$) and a small curvature that causes the E2 transition state to move easily laterally. A plausible position of the transition state and the approximate direction of the reaction coordinate are shown in Figure 2.

**Merging of Mechanisms.** The change in leaving group from $AcO^-$ to $Cl^-$ for **3**-Cl apparently causes a change in mechanism from E1cB to E2. A similar change in mechanism has been found for the oxygen-promoted elimination from $p$-$NO_2PhCH_2CH_2X$ in water/$Me_2SO$ when the leaving group is changed from amine to bromide anion.[43] A change in leaving group from $AcO^-$ to $Cl^-$ does not cause a change in mechanism for the more acidic indene series but, possibly, the bromo compound eliminates by an E2 mechanism.

The reason for the change in mechanism is most likely that the carbanion intermediate is too unstable to exist as a discrete intermediate, i.e., the barrier for expulsion of the leaving group has disappeared. Accordingly, the concerted mechanism is enforced by the change in lifetime of the intermediate. However, as discussed in the introduction, the proton transfer and the cleavage of the bond to the leaving group are to some extent coupled both in the concerted and the stepwise mechanisms.

A change in mechanism can also be induced by making the substrate less acidic. An example is the reaction of **1**-Cl that has a stepwise mechanism, but the corresponding less acidic fluorene substrate **2**-Cl reacts by an E2 mechanism. This shift in mechanism does not seem to be accompanied by a large change in the amount of proton transfer since the $\beta$ values are approximately the same. However, the elimination from $ArCH_2CH_2L^{2+}$ (where the leaving group $L^+$ is DABCO methylated at one of the nitrogens) is followed by a decrease in $\beta$ when passing the mechanistic borderline.[43]

There is another, in principle different, type of change of mechanism. This involves two concurrent mechanisms having different transition-state structures. A change in experimental conditions or structure of the reactants lowers one of the transition states relative to the other that may induce a shift in the major reaction path. Accordingly, the reaction product may, in principal, be formed simultaneously by two parallel reactions. At the borderline, both transition states are of equal energy. Frequently, owing to a large difference in energy of the transition states, one of the mechanisms dominates and is the only mechanism observed. An example is the formation of olefins from **2**-Cl in 25 vol % acetonitrile in water.[24] Parallel E1cB and E1 reactions have been reported recently for the reaction of **1**-Cl with pyridine in methanol.[14]

## Experimental Section

**General.** The high-performance liquid chromatography (HPLC) analyses were carried out with a Hewlett-Packard 1084B liquid chromatograph equipped with a variable-wavelength detector on a C8 reversed-phase column (3.0 × 200 mm) or a CN reversed-phase column (4.6 × 130 mm). The mobile phase was a solution of methanol in water.

(45) Avramovitch, B.; Weyerstahl, P.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 6687–6697.
(46) Koch, H. F.; Dahlberg, D. B.; Lodder, G.; Root, K. S.; Touchette, N. A.; Solsky, R. L.; Zuck, R. M.; Wagner, L. J.; Koch, N. H.; Kuzemko, M. A. *J. Am. Chem. Soc.* **1983**, *105*, 2394–2398.

The reactions were studied at constant temperature in a HETO 01 PT 623 thermostat.

**Materials.** Methanol used for preparation of reaction solutions was of spectroscopic quality, stored over 0.3-nm molecular sieves, otherwise of HPLC grade. *tert*-Butyl alcohol (p.a.) was purified by fractional recrystallization followed by drying over 0.4-nm molecular sieves. Pyridine (p.a.) was dried over KOH and then decanted and distilled from 0.4-nm molecular sieves; the center-cut was collected. Hexamethylenetetramine (Aldrich, Gold Label) was used without further purification. The purification of the other bases has been described previously.[14,20,25] All other chemicals were of reagent grade. Anhydrous sulfuric acid was used to buffer the reaction solutions (Table I and II).

**Substrates.** The syntheses of 9-(2-chloro-2-propyl)fluorene (**2**-Cl), the deuteriated analogue (9-$^2$H)-9-(2-chloro-2-propyl)fluorene (>99.0 atom % $^2$H in the 9 position), and 9-(2-propenyl)fluorene (**5**) have been described recently.[24] The syntheses of 1-(2-chloro-2-propyl)indene (**1**-Cl),[11] 1-(2-bromo-2-propyl)indene (**1**-Br),[13] 9-(acetoxymethyl)fluorene (**3**-OAc),[13] and 9-(chloromethyl)fluorene (**3**-Cl)[25] have also been published.

**Kinetics and Product Studies.** The reaction vessel was a 2-mL HPLC flask sealed with a tight PTFE septum, placed in an aluminum block in the water thermostat, or, in the slower reactions and the reactions at higher temperature, consisted of 1-mL glass ampules. The reactions were initiated by rapid addition of the substrate dissolved in acetonitrile with a microsyringe to the prethermostated base solution in the HPLC flask or to a pear-shaped flask from which the mixed reaction solution was distributed to the glass ampules. The substrate concentration in the reaction solution was usually 0.05 mM in **2**-Cl or **3**-Cl and 0.12 mM in **1**-Cl. At appropriate intervals, samples (200 μL) of the reaction solution were transferred by means of a syringe (in the faster kinetic runs by means of a thermostated water-jacketed syringe) to an HPLC flask containing an appropriate amount of quench solution (prepared by diluting 15.6 mL of 2 M sulfuric acid with 40% ethanol–water to 250 mL) and analyzed. The mol % of the starting material and each of the products were measured, or, in some experiments, the starting material/internal-standard area ratio. The phenomenological rate constants were calculated from plots of ln (mol % starting material) or ln (area ratio) versus time and product data. Acenaphthene was used as internal standard in the kinetic experiments with **3**-Cl.

The samples from the kinetic runs with pyridine were quenched by shaking with a mixture of 700 μL of 1,1,1-trichloroethane, 10 mL of 2 M $H_2SO_4$, and 30 mL of water and ca. 10 g of ice in a 60-mL centrifuge tube. After centrifugation, the organic phase was washed by shaking with about 50 mL of cold water followed by a further centrifugation. The organic phase was then diluted with methanol and analyzed.

The kinetics of the reactions of **1**-Br were studied by UV spectrophotometry. The procedure has been described previously.[25]

Estimated errors are considered as maximum errors derived from maximum systematic errors and random errors.

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**Registry No.** **1**-Br, 75915-20-7; **1**-Cl, 64909-94-0; **2**-Cl, 56954-89-3; **3**-Cl, 36375-77-6; **3**-OAc, 63839-86-1; $D_2$, 7782-39-0.

# Comparative Study of E2 and $S_N2$ Reactions between Ethyl Halide and Halide Ion

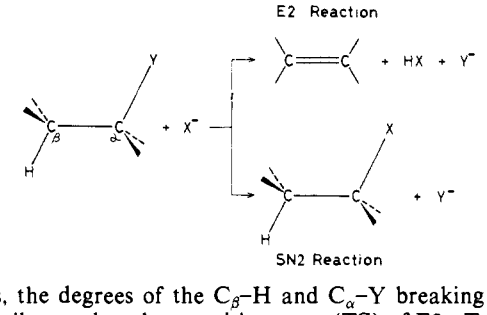
**Tsutomu Minato[1a] and Shinichi Yamabe*[,1b]**

*Contribution from the Yuge Mercantile Marine College, Yuge-cho, Ochi-gun, Ehime 794-25, Japan, and Educational Technology Center, Nara University of Education, Takabatake-cho, Nara 630, Japan.* *Received September 10, 1987. Revised Manuscript Received February 9, 1988*

**Abstract:** The transition-state (TS) geometries of bimolecular nucleophilic eliminations (E2) and substitutions ($S_N2$) between ethyl halides and halide ions are determined with ab initio MO calculations in order to probe the effect of the basicity of nucleophiles and the nucleofugality of the leaving groups on the reaction mechanism. E2 reactions dealt with here are found to the E2H category of the Bunnett's variable TS spectrum. The geometry of the E2 TS is shown to be entirely different from that of the $S_N2$ TS. Although the TS geometries of the syn and anti E2 reactions are calculated to be similar, their activation energies are different according to the extent of the intramolecular charge transfer.

The present paper describes a theoretical study on bimolecular nucleophilic reactions, especially eliminations (E2). There are many experimental studies of base-initiated alkene-forming β eliminations in the condensed phase.[2a-c] E2 reactions are also investigated in the gas phase to examine the intrinsic properties of the isolated systems.[2d-f] A recent study by Fourier transform ion cyclotron resonance mass spectroscopy has shown that the stability of the ion/molecule complex preceding the reaction barrier is important in determining the selectivity of the gas-phase E2.[2f]

E2 is the one-step process involving the simultaneous removal of the β-hydrogen and a leaving group and formation of a double bond. These bond interchanges need not be precisely synchronous.




That is, the degrees of the $C_\beta$–H and $C_\alpha$–Y breaking are not necessarily equal at the transition state (TS) of E2. Two theoretical models, Bunnett's variable E2H TS spectrum[3] and the Winstein–Parker E2C–E2H spectrum,[4] were put forth to deal with

(1) (a) Yuge Mercantile Marine College. Present address: Institute for Natural Science, Nara University, 1500 Misasagi-cho, Nara 631, Japan. (b) Nara University of Education.

(2) (a) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 453 and references cited therein. (b) McLennan, D. J. *Tetrahedron* **1975**, *31*, 2999. (c) Fry, A. *Chem. Soc. Rev.* **1972**, *1*, 163. (d) Doorn, R. V.; Jennings, K. R. *Org. Mass. Spectrom.* **1981**, *16*, 397. (e) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034. (f) Konig, L. J. d.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715.

(3) Bunnett, J. F. *Angew. Chem.* **1962**, *74*, 731.

(4) (a) Parker, A. J.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2240. (b) Parker, A. J. *CHEMTECH* **1971**, *1*, 297.

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