# E2 Elimination of Fluorene Derivatives

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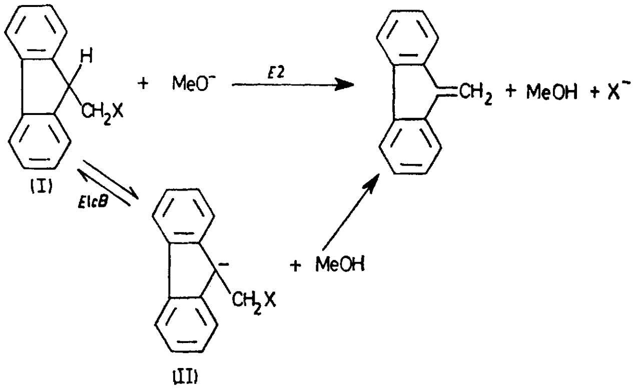
*Summary* Substituent effects on ionisation and E2 elimination of fluorene derivatives indicate a discontinuity between E2 and ElcB reaction paths.

In methanolic sodium methoxide at 25° 9-(hydroxymethyl)-fluorene (I, X = OH) undergoes elimination by an ElcB mechanism.[1] In contrast, for fluorene derivatives with better leaving groups (*e.g.* X = Br, Cl) we find that the rate of elimination exceeds that expected for ionisation to a fluorenyl carbanion, and we infer that the mechanism has changed to E2.

Rates of ionisation of non-eliminating fluorene derivatives (I, X = H, Me, Ph) in methanol at 45° have been determined by Streitwieser from measurements of tritium exchange.[2] Rate constants at 25° may be extrapolated using activation parameters measured for fluorene itself and assuming that substitution does not affect $\Delta S^{\ddagger}$.[3] Correction for the tritium isotope effects, taking 15·4 as the average of measured values,[1,3] yields rate constants for the hydrogen isotopes. Combined with values for X = OH and OMe measured at 25° directly, these may be plotted as log $k$ versus $\sigma^*$ to give a straight line with the normal slope,[4] $\rho^* = 2{\cdot}25$ (Figure, open circles). The constant for X = OMe is too high by a factor of 4 and was omitted from the correlation, but similar behaviour for this substituent has been seen elsewhere.[4a]



Scheme

Rate constants for elimination of fluorene derivatives in which X acts as a leaving group are listed in Table 1. These values are also plotted against $\sigma^*$ (Figure, filled circles) and in all cases the rate constants are greater than those predicted for ionisation, which represent the maximum values for elimination by an ElcB mechanism. For X = Br the difference is large enough (a factor of 145) for an E2 mechanism to be definitely indicated, and there can be little doubt that the same must be true of X = Cl.

Table 1

Observed rate constants for elimination and calculated rate constants for ionisation of 9-(X-methyl)fluorenes.

| X | $\sigma^*$ | $10^2k^a$ (ionisation, calc.) | $10^2k$ (elimination, obs.) | $k$ (elimination) / $k$ (ionisation) |
|---|---|---|---|---|
| Br | 1·02 | 2·63 | 380 | 145 |
| $SO_2Ph$ | 1·24 | 8·22 | 265 | 32 |
| Cl | 1·05 | 3·07 | 64 | 21 |
| SPh | 0·63 | 0·347 | 1·90 | 5·5 |

[a] From $\log k = 2{\cdot}25\sigma^* - 3{\cdot}88$.

The results are of interest in studies of the borderline between concerted and stepwise elimination mechanisms. As discussed earlier,[5] the stability of the fluorenyl carbanion is such that observation of E2 elimination rules out a complete merging of E2 and ElcB reaction paths. The alternative possibility of a merging only of transition states may be examined by comparing substituent effects on the two mechanisms for substrates reacting close to the borderline.

Table 2

Rate depression by α-methyl and α-phenyl substituents in 9-(X-methyl)fluorenes[a]

| α-substituents | Elimination X = Br | Elimination X = Cl | Ionisation X = OH |
|---|---|---|---|
| $H_2$[b] | 1 | 1 | 1 |
| Me, H | 4·5 | 11 | — |
| Ph, H | 12 | 20 | 5·6 |
| $Me_2$ | 92 | 470 | 44 |

[a] Substituents α to the group X; figures denote decrease in rate relative to unsubstituted substrate. [b] Correcting for the tritium isotope effect (for X = OH), relative rates, Br:Cl:OH, are 1530:260:1. Primary β-deuterium isotope effects for X = Cl and X = OH are $k_H/k_D$ = 6·4 and 6·5 respectively.

The effects of methyl and phenyl substituents α to the leaving group for E2 elimination and for ionisation to a fluorenyl carbanion are compared in Table 2. The rate of ionisation was measured from exchange of a tritium label and represents the rate-determining step of an ElcB elimination involving a reactive leaving group. It is clear that both reactions are retarded by α-substituents, and the qualitative similarity of the effects seems to indicate quantitative differences in transition-state structure rather than a mechanistic discontinuity. Measurements of hydrogen isotope effects also yield similar values (*e.g.* footnote b of Table 2), and it can be seen from the Figure that changes in the leaving group affect the rates of elimination by factors not much greater than those expected in the ionisation.

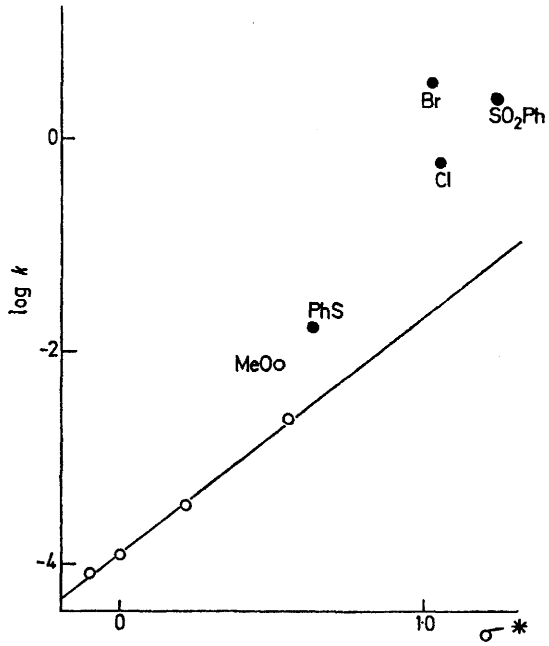


Figure. Plot of log $k$ versus $\sigma^*$ for ionisation (○) and elimination (●) of 9-(X-methyl)fluorenes in methanolic NaOMe at 25°.

On the other hand the relative magnitudes of the α-substituent effects do not fall in the sequence of leaving group reactivities: Br > Cl > OH. This suggests that at the point of mechanistic change, E2 and ElcB transition states, although similar in structure, are not identical.

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[1] R. A. More O'Ferrall, *J. Chem. Soc. B*, 1970, 268.

[2] A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, 1967, **89**, 693.

[3] A. Streiswieser, Jr., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

[4] (a) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, 1967, **89**, 5911; (b) P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 817.

[5] R. A. More O'Ferrall, *J. Chem. Soc., B*, 1970, 274.