Chlorine Isotope Effects in Dehydrochlorination. A Mechanistic Crossover at the *E*1c*B*-*E*2 Borderline Induced by a Change in *para*-Substituent

By Alan Grout, Duncan J. McLennan,* and Irving H. Spackman
(*Department of Chemistry, University of Auckland, Auckland, New Zealand*)

Summary Chlorine isotope effects in base-promoted dehydrochlorinations have been measured for the first time, and the results point to an *E*2 to *E*1c*B* mechanistic switch in the *para*-substituted $(p\text{-}YC_6H_4)_2CH{\cdot}CHCl_2$ series, as the substituent becomes more powerfully electron-withdrawing.

The borderline area between concerted (*E*2) and carbanionic (*E*1c*B*) mechanisms of β-elimination is a subject of current interest,[1] and an important object is to delineate the variation of structure and environment required to facilitate the operation of one mechanism or the other. To date there has been no evidence that alteration of *para*-substituents in the Ar–CH–CX skeleton causes a mechanistic crossover in the base-promoted elimination of HX.

In the Figure are shown Brönsted plots, based on pK_a estimates, for the NaOMe–MeOH induced dehydrochlorinations of substrates in the (p-$YC_6H_4)_2CH{\cdot}CCl_3$ (DDT) and (p-$YC_6H_4)_2CH{\cdot}CHCl_2$ (DDD) series.[2,3] It is believed that the former react *via* an *E*1*cB* process (rate-limiting proton transfer)[2] whilst the latter undergo *E*2 elimination since the dehydrochlorination rates are higher than the calculated rates for carbanion formation, as established by the DDT line.[3] Recent measurements have shown that the reactivity of (p-$NO_2C_6H_4)_2CH{\cdot}CHCl_2$ [filled triangle in the Figure; k_2 (30 °C) 0·481 l mol^{-1} s^{-1}] places it in the *E*1*cB* category, but such a mechanistic assignment is as uncertain as are the pK_a estimates.

TABLE

Intramolecular[a] chlorine isotope effects for dehydrochlorination of (p-$YC_6H_4)_2CH{\cdot}CHCl_2$ compounds by NaOMe–MeOH at 30 °C.

Y	k_{35}/k_{37}[b]
NO_2	0·99995
Cl	1·00232
H	1·00354
MeO	1·00379

[a] Calculations (ref. 6) indicate k_{35}/k_{37} (intra.) = *ca.* k_{35}/k_{37} (inter.). [b] Uncertainties < ± 0·00026. Isotopic ratios of derived methyl chloride (J. W. Taylor and E. P. Grimsrud, *Analyt. Chem.*, 1969, **41**, 805) were measured on a Varian MAT CH7 mass spectrometer equipped with a double inlet system and twin Faraday cup detectors (positive ion collection).

Thus we have measured leaving group chlorine isotope effects for compounds in the DDD series (Table). These are intramolecular isotope effects for decomposition of $Ar_2CH{\cdot}CH^{35}Cl^{37}Cl$. The results firstly support the contention that the *E*1*cB* mechanism prevails for Y = NO_2, since no isotope effect is observed. This also means that no isotope effect attends decomposition of the carbanion to products, so this step must be extremely rapid, with a transition state which is most carbanion-like. However, the rate cannot be at the vibrational limit, as distinction between *E*2 and *E*1*cB* is lost at that point.

For substrates with less powerfully electron attracting *para*-substituents, the *E*2 mechanism is clearly operative. The trend in k_{35}/k_{37} with increasing σ is intelligible in terms of current theories of *E*2 transition state structure[1c,4] and parallels a trend reported for the $ArCH_2{\cdot}CH_2NMe_3^+$ series.[5] The k_{35}/k_{37} values are small compared with most chlorine leaving group isotope effects, and are consistent with those from model cut-off calculations based on transition state structures having $C_\alpha \cdots\cdots Cl$ partial bonds substantially less than half-broken.[6]

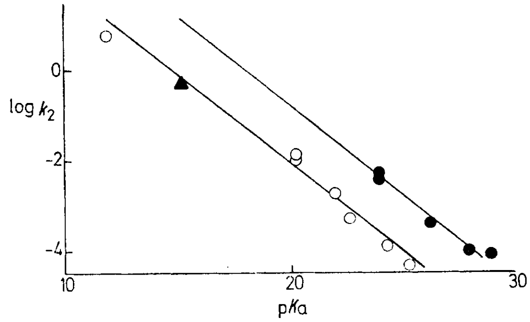

FIGURE. Brönsted plots of log k_2 for dehydrochlorination of *para*-substituted DDT compounds (open circles), DDD compounds (filled circles), and (p-$NO_2C_6H_4)_2CH{\cdot}CHCl_2$ (filled triangle) against pK_a values based on pK_a = 33·45 for Ph_2CH_2 (see ref. 2).

An all-*E*1*cB* explanation is superficially attractive. It could be argued that the Y groups influence the rate of carbanion decomposition to olefin and Cl^-, and hence they likewise influence the character of the transition state with respect to $C_\alpha \cdots\cdots Cl$ rupture and thus the magnitude of the isotope effect. In terms of Hammond's postulate,[7] the carbanions should become more stable as σ increases, the decomposition should become more activation-controlled, the transition state should thus become less carbanion-like, and k_{35}/k_{37} should increase. This is contrary to fact.

The *E*2 reactions in the DDD series are as close to the *E*2–*E*1*cB* borderline as any that have been studied. A structural alteration as subtle as a change in *para*-substituent is thus sufficient to tip the balance in favour of the *E*1*cB* mechanism.

(*Received, 5th July* 1976; *Com.* 753.)

---

[1] (a) F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374; (b) W. H. Saunders, *ibid.*, 1976, **9**, 19; (c) R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274.

[2] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 1373.

[3] A. B. N. Gray and D. J. McLennan, *J.C.S. Perkin II*, 1974, 1377.

[4] D. A. Winey and E. R. Thornton, *J. Amer. Chem. Soc.*, 1975, **97**, 3102.

[5] P. J. Smith and A. N. Bourns, *Canad. J. Chem.*, 1974, **52**, 749.

[6] G. W. Burton, L. B. Sims, and D. J. McLennan, unpublished calculations. See also W. H. Saunders, *Chem. Scripta*, 1975, **8**, 27.

[7] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.