MNDO SCF-MO Calculations of Kinetic Isotope Effects for Dehydrochlorination Reactions of Chloroalkanes

By Henry S. Rzepa

(*Department of Chemistry, Imperial College, London* SW7 2AY)

Summary Calculations of $^{1}H/^{2}H$, $^{12}C/^{13}C$, and $^{35}Cl/^{37}Cl$ kinetic isotope effects using the MNDO SCF-MO method suggest that the transition states for the gas-phase dehydrochlorination of chloroalkanes differ significantly from some previously suggested models.

Although it is generally agreed that many gas-phase dehydrochlorinations are concerted reactions,[1] several models for the four-centred transition state which differ in the extent to which each bond is broken or formed have been proposed.[2,3] One way these models can be assessed is by their ability to reproduce kinetic isotope effects (KIE) observed for these reactions. The calculation of KIE requires the structures and the vibrational frequencies of both the reactant and the transition state[4] and those for the latter in particular have proved to be a major problem, since they cannot be directly measured and have to be estimated by making numerous and rather arbitrary approximations. Quantum mechanical calculations can in principle provide one solution to this problem, although to date there have been very few such applications to systems as complex as the title reaction.[5] Reported here are the results of MNDO SCF-MO calculations,[6] which indicate that the transition states for these reactions may have significantly different structures from some previously proposed models.[2,3]

The geometries of chloroethane (**1**), 2-chloro-2-methylpropane (**2**), and 1-methoxychloroethane (**3**) were completely

CH_3CH_2Cl (**1**)
$(CH_3)_3CCl$ (**2**)
$CH_3CH(OCH_3)Cl$ (**3**)

optimised using the Davidon–Fletcher–Powell method[6] and the corresponding respective transition states (**4**)—(**6**) for the elimination of HCl were located by minimising the sum of the squared scalar gradients,[7] using the standard MNDO method with an s/p valence orbital basis set. The calculated force constant matrices for (**4**)—(**6**) had just one negative eigenvalue[8] and an associated eigenvector which corresponded to the correct reaction co-ordinate (Figure). The calculated geometry of (**4**) (Figure) is similar to that predicted by the *ab initio* STO-3G results obtained by Hiberty[9] and *ab initio* 4-31G calculations for the analogous reaction of fluoroethane.[10] It differs strikingly from models suggested by Maccoll[2] or Setzer,[3] in which the C–Cl bond is only stretched slightly and the C–H bond is largely cleaved in the transition state. Electron-releasing substituents are calculated to stabilise the incipient carbonium ion in the transition state, increasing the C–Cl bond length and decreasing the frequency of the imaginary mode and the enthalpy of activation (Table). The latter are uniformly

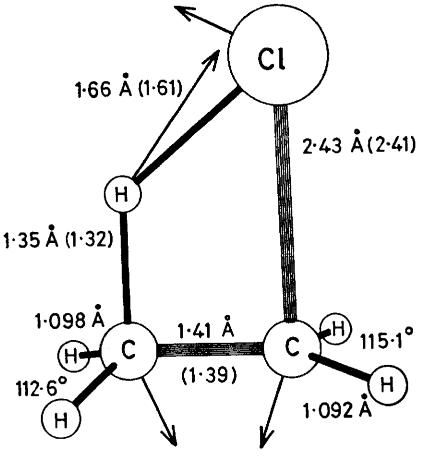

Figure. Scale plot of the transition state (**4**) calculated for the dehydrochlorination of (**1**), with arrows indicating the calculated form of the reaction co-ordinate (no mass weighting). Bond lengths shown in parentheses are those calculated by Hiberty.[9]

TABLE. Calculated (observed) properties for dehydrochlorination reactions of chloroalkanes.

Property	(**1**)	(**2**)	(**3**)
$\Delta H^{\circ}/(\mathrm{kJ/mol})^{a}$	115 (72)	60 (73)	95
$\Delta H^{\ddagger}/(\mathrm{kJ/mol})^{b}$	325 (235 ± 2·8)	272 (186 ± 2·4)	249 (135 ± 3·0)
$\Delta r_{\mathrm{C-Cl}}{}^{c}$	+34·8	+45·5	+54·1
$\Delta r_{\mathrm{C-H}}{}^{c}$	+21·5	+11·5	+10·8
$\Delta\alpha^{d}$	−23·6	−25·5	−30·0
$\nu_1{}^{e}$	2113	1560	947
$k^{35}/k^{37\,f}$	1·0021 (1·0016)$^{668\,\mathrm{K}}$	1·0036 (1·0090)$^{523\,\mathrm{K}}$	1·0058$^{400\,\mathrm{K}}$
	1·0017 (1·0015)$^{754\,\mathrm{K}}$	1·0027 (1·0082)$^{616\,\mathrm{K}}$	1·0041$^{500\,\mathrm{K}}$
$k^{\mathrm{H}}/k^{\mathrm{D}\,g}$	3·02	2·57	2·46
$k^{12}/k^{13}_{\mathrm{CH}}{}^{h}$	1·0012$e^{3\cdot19/T}$	1·0023$e^{2\cdot66/T}$	1·0027$e^{2\cdot78/T}$
$k^{12}/k^{13}_{\mathrm{CCl}}{}^{h}$	0·9985$e^{4\cdot49/T}$	1·0003$e^{2\cdot63/T}$	1·0007$e^{0\cdot83/T}$

[a] Enthalpy of reaction. Experimental values from J. B. Pedley and J. Rylance, 'Sussex - N. P. L. Computer Analysed Thermochemical Data,' University of Sussex, 1977. [b] Data from sources cited in ref. 1 and re-analysed using the Eyring equation. [c] Percentage change of bond length in the transition state. [d] Percentage change in the CCCl bond angle in the transition state. [e] Frequency corresponding to the reaction co-ordinate, in cm^{-1}. [f] Chlorine kinetic isotope effects, from ref. 2. [g] Calculated harmonic rate ratios for the [^{2}H$_1$]-species at 500 K. [h] Approximate temperature dependence of the calculated HRR for the ^{13}C substituted species.

too high by about 100 kJ/mol, a result similar to that obtained by Hiberty.[9]

Harmonic rate ratios (HRR)[4] for the reaction of (**1**), obtained from the calculated[8] vibrational frequencies of the ^{35}Cl and ^{37}Cl isotopically substituted reactant and transition state, are very similar to the high-pressure limit chlorine KIE measured by Maccoll and his co-workers.[2] The observed gas-phase chlorine KIE for (**2**) are much larger than the calculated rate ratios (Table), although the latter are very similar to the KIE found for the solvolysis of (**2**) in solution (obs.,[11] 1·0109 at 283 K; MNDO calc., 1·0101). These large observed chlorine KIE for the gas-phase reaction of (**2**) have been attributed[2] to a large temperature independent factor[4] (ν_i^{35}/ν_i^{37} = 1·0061; MNDO calc., 1·0005), which suggests that a relatively small gas-phase deuterium KIE should be expected for this particular reaction. Such measurements have not been made for (**2**) or (**3**) but they have been reported for the [^{2}H$_4$]-derivative of (**1**). The observed[12] temperature dependence [$k^{\mathrm{H}}/k^{\mathrm{D}}$ = 1·16 exp$(985/RT)$] compares well with the calculated behaviour for (**1**) [$k^{\mathrm{H}}/k^{\mathrm{D}}$ = 1·04 exp$(1048/RT)$]. The predicted deuterium KIE for (**2**) and (**3**), although smaller than those for (**1**), are nevertheless substantial primary effects (Table). The ^{12}C/^{13}C HRR for isotopic substitution at the carbon atom bearing either the departing chlorine or the departing hydrogen atom are predicted to be similar in magnitude, although they have significantly different temperature behaviour (Table).

These results demonstrate that SCF-MO calculations may provide a more rational basis for interpreting kinetic isotope effects than the reverse procedure of attempting to establish a transition state model from the observed kinetic data.

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