Use of Kinetic Isotope Effects in Mechanism Studies. 4.[1] Chlorine Isotope Effects Associated with Alkoxide-Promoted Dehydrochlorination Reactions

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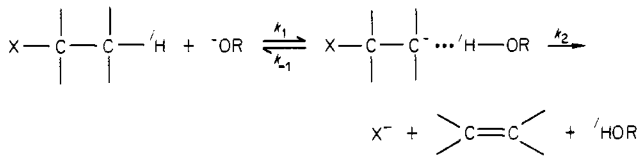
Abstract: The method of measuring k^{35}/k^{37} for the alkoxide-promoted deprotiochlorination and dedeuteriochlorination reactions has been applied to $C_6H_5C^{\prime}H(CH_3)CH_2Cl$ (I-Cl), $C_6H_5C^{\prime}HClCH_2Cl$ (V), and $C_6H_5C^{\prime}HClCF_2Cl$ (III). For reactions occurring with ethanolic sodium ethoxide the following values for k^{35}/k^{37} have been measured: I-Cl-*h*, 1.005 90 + 0.000 13, and I-Cl-*d*, 1.005 07 ± 0.000 36 at 75 °C; V-*h*, 1.009 08 ± 0.000 08, and V-*d*, 1.007 34 ± 0.000 12 at 24 °C; III-*h*, 1.012 29 ± 0.000 47, and III-*d*, 1.010 03 ± 0.000 24 at 0 °C. Methanolic sodium methoxide promoted eliminations gave similar results for V and III: V-*h*, 1.009 78 ± 0.000 20, and V-*d*, 1.007 76 ± 0.000 20 at 21 °C; III-*h*, 1.012 55 ± 0.000 48, and III-*d*, 1.010 25 ± 0.000 43 at 20 °C. The results for I-Cl are most consistent with an E2 mechanism, while the results for III and V suggest a multistep reaction sequence. The Arrhenius behavior of ethoxide-promoted dehydrochlorination of V-*h* gives a good linear correlation between −10 and 50 °C, with an $E_a{}^H = 21.26 \pm 0.05$ kcal/mol and $\ln A^H = 29.29 \pm 0.09$. Rate constants measured for 55, 60, 65, and 70 °C show increasing negative deviation from the slope. Similar behavior was not observed for V-*d* which resulted in $E_a{}^D = 21.57 \pm 0.28$ and $\ln A^D = 28.37 \pm 0.28$ when rate constants over a 50 °C range (20–70 °C) were used. The $\Delta E_a{}^{D-H} = 0.31$ and $A^H/A^D = 2.5$ for an observed $k^H/k^D = 4.24$ at 25 °C were similar for results obtained for III. The possibility that the high values of k^{35}/k^{37} for both III and V could result from a chlorine isotope effect associated with the proton transfer step of an E1cB mechanism is discussed.

A hydron transfer reaction occurring with a moderate amount of internal return can result in temperature dependence for primary kinetic isotope effects similar to those obtained from a proton transfer reaction thought to occur with quantum-mechanical tunneling.[3] Therefore, we have been able to computer simulate the excellent experimental data reported by Shiner et al.[4] for the ethoxide-promoted dehydrobromination of $C_6H_5C^{\prime}H(CH_3)CH_2Br$ (I-Br) for all three isotopes over their entire temperature range by assuming an internal return mechanism (Scheme I). Since this type of Arrhenius behavior is cited as experimental evidence for the need of a tunneling correction, we initiated studies designed to distinguish between the two interpretations. An elimination reaction offers additional methods which can be used to determine whether experimental data are consistent with a one-step or a two-step process, namely leaving group isotope effects[5] and element effects.[6]

Although the primary kinetic isotope effect $k^H/k^D = 7.82$ at 25 °C appears quite normal and does not suggest the necessity for a tunneling correction, the corresponding differences in Arrhenius parameters reported for I-Br, $\Delta E_a{}^{D-H} = 1.77$ kcal mol^{-1} and $A^H/A^D = 0.40$, fit current theories on tunneling behavior. Kaldor and Saunders[7] suggest that this type of phenomenon can arise in an E2 mechanism from a contribution of heavy-atom motion to the motion along the reaction coordinate, which keeps the semiclassical isotope effects normal or small. Thus, "normal" k^H/k^D values in E2 reactions are not inconsistent with the need for a tunneling correction. Conversely, some abnormal k^H/k^D values and Arrhenius parameters for E2-like reactions can be rationalized without recourse to tunneling,[8] and the interpretation of such results is not completely clear-cut. Since the temperature dependence and magnitude of the isotope effects for I–Br can also be consistent with an internal return mechanism,[9] we sought experimental methods to distinguish between the two alternative reaction pathways.

Scheme I



The Arrhenius behavior and primary kinetic isotope effects observed for ethoxide-promoted dehydrochlorination of $C_6H_5C^{\prime}H(CH_3)CH_2Cl$ (I-Cl) are similar to those reported for I-Br. Both an E2 mechanism and the E1cB pathway with internal return should give a measurable $^{35}Cl/^{37}Cl$ leaving group isotope effect;[10] however, measuring k^{35}/k^{37} for both the protio and deuterio compounds should in principle allow for experimental differentiation between the two alternative mechanisms.[1,3]

The rather large element effect, I-Cl:I-Br = 1.0:64 at 50 °C, coupled with the substantial isotope effects, k^H/k^D greater than 6 at 50 °C, should be convincing evidence that there is cleavage of both C–H and C–X bonds in what would be an E2 transition state;[11] however, we have observed k^H/k^D values of 2–4 for alkoxide-promoted dehydrohalogenations which appear not to proceed by a simple E2 mechanism and yet give k^{Br}/k^{Cl} rate ratios of 25–50.[12] This has led us to doubt the validity of using element effects to assign mechanisms to elimination reactions.

Another argument against a two-step mechanism for systems similar to I-Br is that the rate of elimination is much faster than

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[1] Part 3: Koch, H. F.; Koch, J. G.; Tumas, W.; McLennan, D. J.; Dobson, B.; Lodder, G. *J. Am. Chem. Soc.* **1980**, *102*, 7955–7956.

[2] (a) Ithaca College. (b) University of Auckland.

[3] Koch, H. F.; Dahlberg, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6102–6107.

[4] (a) Shiner, V. J., Jr.; Smith, M. C. *J. Am. Chem. Soc.* **1961**, *83*, 593–598. (b) Shiner, V. J., Jr.; Martin, B. *Pure Appl. Chem.* **1964**, *8*, 371–378.

[5] An excellent review article regarding the use of various isotope effects has been written (by Fry, A. *Chem. Soc. Rev.* **1972**, *1*, 163–210).

[6] Bunnett, J. F.; Garbisch, E. W., Jr.; Pruitt, K. M. *J. Am. Chem. Soc.* **1957**, *79*, 385–391.

[7] Kaldor, S. B.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7594–7599.

[8] McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1753–1758.

[9] One can calculate an internal-return value, $a^H = k_{-1}/k_2 = 0.4$, from the kinetic data from all three isotopes of I-Br.

[10] Grout, A.; McLennan, D. J.; Spackman, I. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1758–1763.

[11] Bordwell, F. G. *Acc. Chem. Res.* **1972**, *5*, 377.

[12] Koch, H. F.; Dahlberg, D. B.; McEntee, M F.; Klecha, C. J. *J. Am. Chem. Soc.* **1976**, *98*, 1060–1061.

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Table I. Chlorine and Hydrogen Isotope Effects, and Element Effects for Sodium Alkoxide Promoted Dehydrochlorination Reactions in Alcohol

compd[a]	solvent	k^{35}/k^{37} (°C)	k^H/k^D (°C)	k^{Br}/k^{Cl} (°C)
I-Cl-h	EtOH	1.00590 ± 0.00013 (75)	5.37 (75)	52 (75)
I-Cl-d	EtOH	1.00507 ± 0.00036 (75)		55 (75)
IV	EtOH	1.00580 ± 0.00034 (75)	5.59 (75)	44 (75)
V-*h*	EtOH	1.00908 ± 0.00008 (24)	4.06 (25)	27 (25)[b]
V-*d*	EtOH	1.00734 ± 0.00012 (24)		24 (25)[b]
V-*h*	MeOH	1.00978 ± 0.00020 (21)	3.25 (25)	31 (25)[b]
V-*d*	MeOH	1.00776 ± 0.00020 (21)		24 (25)[b]
III-*h*	EtOH	1.01229 ± 0.00047 (0)	2.94 (0)	
III-*d*	EtOH	1.01003 ± 0.00024 (0)		
III-*h*	MeOH	1.01255 ± 0 00048 (20)	2.28 (25)	49 (25)[c]
III-*d*	MeOH	1.01025 ± 0.00043 (20)		29 (25)[c]

[a] I-Cl = $C_6H_5C^iH(CH_3)CH_2Cl$, III = $C_6H_5C^iHClCF_2Cl$, V = $C_6H_5C^iHClCH_2Cl$, IV = $C_6H_5CH_2CH_2Cl$. [b] V is compared to $C_6H_5C^iHBrCH_2Br$. [c] III is compared to $C_6H_5C^iHBrCF_2Br$.

the expected proton transfer reaction as predicted by pK_a differences between the carbon acid and the conjugate acid of the base used to promote the elimination reaction.[13] We will address this problem in depth in a future paper and merely state that such an argument is not conclusive.[14] That paper will include measured α-carbon isotope effects for the I-X series as well as the measured hydrogen isotope effects on k^{12}/k^{14} for both I-I and I-Cl. These observed k^{12}/k^{14} values range from 1.028 and 1.034 at 50 °C and are independent of halide or hydrogen isotope. The conclusions drawn from the α-carbon and chlorine isotope effects (I-Cl) appear to support the widely held belief that the 2-phenyl-1-halopropane system undergoes alkoxide-promoted dehydrohalogenation via an E2 mechanism.

Results and Discussion

Chlorine Isotope Effects for $PhC^iH(CH_3)CH_2Cl$ and $PhCH_2CH_2Cl$. Both an E2 mechanism and the E1cB pathway with internal return should give a measurable $^{35}Cl/^{37}Cl$ leaving group isotope effect;[10] however, measuring k^{35}/k^{37} for both protio and deuterio compounds should allow for experimental distinction between the two alternative mechanisms.[3] If the ethoxide-promoted elimination of I–Cl proceeds via an E1cB mechanism with a moderate amount of internal return, there should be a dramatic difference in the observed k^{35}/k^{37} for I-Cl-*h* vs. I-Cl-*d*. Since rates of elimination for I-Cl-*t* have not been measured, we are unable to calculate the internal-return parameters necessary to predict k^{35}/k^{37} for I-Cl-*h* and I-Cl-*d* under E1cB conditions. However, the parameters used to model the reported data for I-Br-^{i}H can be used to calculate an approximate value of k^{35}/k^{37} = 1.003 70 for I-Cl-*h*.[15] This value should be readily distinguished from the expected maximum value of 1.013 60[15b] since the precision of $^{35}Cl/^{37}Cl$ measurements allows for calculation of k^{35}/k^{37} rate ratios to within 10–30 parts per 10^5.[10] In this model the competition between the return step and forward step, k_{-1}/k_2 in Scheme I, favors k_2 by a factor of only 2.5, and it is not surprising that an appreciable chlorine isotope effect could be observed. However, when reaction occurs with I-Cl-*d*, k_2 would be favored by a factor of 25 and this should result in a rather large drop in the chlorine isotope effect, k^{35}/k^{37} = 1.000 50. Again, the two values, 1.003 70 and 1.000 50, should be experimentally distinguishable.

The osberved k^{35}/k^{37} = 1.005 90 at 75 °C (see Table I) for ethoxide-promoted elimination of I-Cl-*h* coupled with the k^{35}/k^{37} value of 1.005 07 for I-Cl-*d* provides experimental evidence that favors an E2 pathway for this dehydrochlorination reaction. Based on calculations described in ref 3 and the observed value for I-Cl-*h*, a value for k^{35}/k^{37} of only 1.000 90 for I-Cl-*d* was anticipated if reaction proceeded by an E1cB pathway.

There is a similarity in the magnitude of primary kinetic isotope effects for β-phenethyl halides and 2-phenyl-1-propyl halides,[14b] and this is also observed for chlorine isotope effects. The k^{35}/k^{37} of 1.005 80 measured for $C_6H_5CH_2CH_2Cl$ (IV) is virtually the same as that observed for I-Cl-*h* at 75 °C. Reaction of IV with ethanolic sodium ethoxide results in 4–5% substitution competing with the elimination reaction. Therefore, chlorine isotope effects were not measured with $C_6H_5CD_2CH_2Cl$, since substitution now accounts for ca. 25% of the reaction product. Since reaction of I-Cl-*d* also results in 3–4% substitution, part of the difference in the observed k^{35}/k^{37} for I-Cl-*h* compared to I-Cl-*d* might arise from this competing substitution rather than elimination of chloride.

Isotope Effects for PhC^iHClCF_2Cl. We have encountered an unusual Arrhenius behavior of isotope effects for $C_6H_5C^iHBrCF_2Br$ (II) and $C_6H_5C^iHClCF_2Cl$ (III) which is clearly not in accordance with a simple E2 mechanism.[12,16,17] Studies on both systems have continued and temperature ranges were extended. New results for III with both methoxide and ethoxide are found in Table II. The activation parameters are only slightly changed from those reported in ref 12, and the almost temperature-independent nature of the isotope effects remains. Although this type of Arrhenius behavior is possible from a reaction proceeding by an internal-return mechanism,[3] we have not been able to model the behavior of all three isotopes of either II or III by assuming a simple two-step pathway as shown in Scheme I.

In an attempt to better understand this reaction, we employed the technique of using both III-*h* and III-*d* for measuring chlorine isotope effects. Experimental results are summarized in Table I. Methanolic sodium methoxide promoted dehydrochlorination resulted in k^{35}/k^{37} values of 1.012 55 ± 0.000 48 (III-*h*) and 1.010 25 ± 0.000 43 (III-*d*) at 20 °C. The difference between III-*h* and III-*d* is well outside experimental uncertainty; however, based on the value obtained for III-*h*, a value for k^{35}/k^{37} of only 1.003 00 to 1.006 00 for III-*d* was anticipated. Therefore, the experimental difference is much smaller than expected. Since reaction with sodium ethoxide is 17 times faster than elimination using methoxide, k^{35}/k^{37} values were obtained at 0 °C in ethanol. The observed values of 1.012 29 ± 0.000 47 (III-*h*) and 1.010 03 ± 0.000 24 (III-*d*) are within experimental uncertainty of the corresponding effects in methanol even though k^H/k^D differs in the two solvents, 2.3 (MeOH) and 2.8 (EtOH) at 0 °C. These results appear to confirm our previous suspicions that alkoxide-promoted eliminations in the $ArCHXCF_2X$ series are neither a concerted mechanism nor are they a simple E1cB pathway with internal return (Scheme I).

It is conceivable that the anomalous Arrhenius behavior of the hydrogen isotope effects could arise from contributions from competing pathways having different isotope effects and temperature dependences. One can rule out a competing E1 mechanism since ionization of CF_2X to form CF_2^+ and X^- is highly

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(13) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 21–22.

(14) (a) Koch, H. F.; Lodder, G.; Tumas, W.; Koch, N. H.; Evans, J. C., paper in preparation. (b) Observed values for k^H/k^D at 50 °C are 6.0 (I-I) and 6.3 (I-Cl) which can be compared to literature values of 6.2 (I-Br)[4b] and 6.0 ($PhC^iH_2CH_2Br$).[14c] (c) Saunders, W. H., Jr.; Edison, D. H. *J. Am. Chem. Soc.* **1960**, *82*, 138–142.

(15) (a) Reference 3, p 6105. In those calculations, we assumed a maximum C–Cl bond breaking in the transition state and values are much higher than one would expect to observe; however, the sharp drop in values going from the protium to the deuterium compound is still predicted. (b) It must be realized that the model values of k^{35}/k^{37} quoted are sensitive to initial parameters, principally the figure of 8 kcal mol^{-1} used for $E_2^{37} - E_2^{35}$, and are therefore to be regarded as indicative rather than as literal values for chlorine isotope effect maxima.

(16) Kinetic studies in our laboratory on similar systems suggest that bromine and chlorine attached to the potential carbanion site behave almost identically. Examples are cited in ref 12.

(17) (a) The results for $ArCHXCF_2X$ have been cited as the only cases of elimination reactions that contrast markedly from the apparent E2 pattern exemplified by results reported by Kaldor and Saunders[7] and observed for I-X.[4,14] (b) Kwart and Horgan (Kwart, H.; Horgan, A. G. *J. Org. Chem.* **1982**, *47*, 159–161 have recently reported that a deactivated analogue of I, namely $PhCHDCBr(CH_3)CO_2CH_3$, gives a temperature-independent PKIE of $(k^H/k^D)_{obsd}$ = 1.227. (c) Thibblin et al. (Thibblin, A.; Onyido, I.; Ahlberg, P. *Chem. Scr.* **1982**, *19*, 145–148) report that amine-promoted 1,4-elimination of acetic acid from 3-(2-acetoxy-2-propyl)indene and its *1,1*-d_2 substituted analogue gives temperature-independent PKIE of $(k^H/k^D)_{obsd}$ = 1.66 (quinuclidine in MeOH from 0–50 °C) and 2.77 (triethylamine in acetonitrile/water from 0–40 °C).

Table II. Arrhenius Parameters and Isotope Effects for Alcoholic Sodium Alkoxide Promoted Dehydrohalogenations

	$C_6H_5C^iHClCF_2Cl$		$C_6H_5C^iHClCH_2Cl$	
	EtOH	MeOH	EtOH	MeOH
k^H, M^{-1} s^{-1}, 50 °C		2.69×10^{-1}	2.23×10^{-2}	2.31×10^{-3}
25 °C	2.21×10^{-1}	1.75×10^{-2}	1.39×10^{-3}	1.25×10^{-4}
0 °C	1.14×10^{-2}	6.87×10^{-4}	5.22×10^{-5}	
temp range, °C	−20 to 15	−5 to 50	−10 to 50	25 to 70
E_a^H, kcal/mol	19.17 ± 0.15	20.95 ± 0.10	21.26 ± 0.05	22.38 ± 0.22
$\ln A^H$	30.84 ± 0.28	31.30 ± 0.18	29.29 ± 0.09	28.77 ± 0.36
k^D, M^{-1} s^{-1}, 50 °C		1.17×10^{-1}	5.47×10^{-3}	6.71×10^{-4}
25 °C	8.09×10^{-2}	7.64×10^{-3}	3.28×10^{-4}	3.26×10^{-5}
0 °C	4.11×10^{-3}	3.03×10^{-4}	1.17×10^{-5}	
temp range, °C	−15 to 25	0 to 50	20 to 70	30 to 75
E_a^D, kcal/mol	19.30 ± 0.10	20.90 ± 0.10	21.57 ± 0.18	23.17 ± 0.18
$\ln A^D$	30.04 ± 0.18	30.40 ± 0.17	28.37 ± 0.28	28.77 ± 0.28
k^H/k^D, 50 °C		2.30	4.08	3.44
25 °C	2.73	2.29	4.24	3.83
0 °C	2.77	2.27	4.46	
ΔE_a^{D-H}	0.13	−0.05	0.31	0.79
A^H/A^D	2.2	2.5	2.5	0.99

unlikely; however, syn and anti eliminations come to mind in this regard. Studies on methoxide-promoted elimination of $C_6H_5C^iHBrCFClBr$ suggest that these reactions are completely anti-stereospecific.[18] Furthermore, the product distribution for $C_6H_5CHBrCFBr_2$ and $C_6H_5CDBrCFBr_2$ remains constant at 85:15 for the *E*:*Z* ratio of $C_6H_5CBr{=}CFBr$ over a 20 °C temperature range. The k^H/k^D values for the reactions producing the isomeric alkenes are thus identical over this range.[18] Future papers will deal with this question in greater detail.

Isotope Effects for PhC^iHClCH_2Cl. The behavior of hydrogen and chlorine isotope effects for the alkoxide-promoted dehydrochlorination of $C_6H_5C^iHClCH_2Cl$ (V) becomes important since the reactivity of V falls between $C_6H_5CH(CH_3)CH_2Cl$ (I-Cl) and $C_6H_5CHClCF_2Cl$ (III) and the chloride leaves from CH_2Cl rather than from CF_2Cl. Initial Arrhenius behavior of the observed hydrogen isotope effects for the ethoxide-promoted eliminations of V-*h* and V-*d* appeared quite normal with the values of ΔE_a^{D-H} (1.02 kcal/mol) and A^H/A^D (0.73) well within limits of current theories for isotope effects. Therefore the observed value of $k^H/k^D = 4.2$ at 25 °C could result from an E2 pathway with an asymmetric transition state that has residual zero-point energy. However, it is important to note that we have been able to model this type of behavior with an ElcB mechanism that features internal return.[19]

The intitial values for E_a^H (20.71 ± 0.15 kcal/mol) and $\ln A^H$ (28.37 ± 0.24) were calculated from a plot of ln *k* vs. 1/*T* using rate constants measurd at 5 °C intervals over a temperature range of 10–65 °C.[20] Although the slope was calculated with $r = 0.9997$, a close inspection showed that only the end temperatures (10, 15, 55, 60, 65) gave appreciable negative deviations from the line. Because of this apparent slight curvature, it was decided to extend the temperature range to cover −10 to 70 °C.[21] The new Arrhenius plot confirmed our suspicion that there is indeed a break in the slope. This break is in the wrong direction to suggest that it results from a change in mechanism. By use of the range −10 to 50 °C, values for $E_a^H = 21.26 \pm 0.05$ kcal/mol and $\ln A^H = 29.29 \pm 0.09$ are obtained and the observed rate constants at higher temperatures show a progressively greater negative deviation from those predicted by extrapolation to 55 °C (−9%), 60 °C (−12%), 65 °C (−15%), and 70 °C (−18%). Arrhenius parameters calculated with the observed rate constants between 50 and 70 °C are much different, $E_a^H = 18.9 \pm 0.4$ kcal/mol and $\ln A^H = 25.6 \pm 0.6$, than those calculated from the 10–65 °C or −10 to 50 °C plots.

The Arrhenius plot for V-*d* using the temperature range 20–70 °C does not show a behavior similar to that observed for V-*h*, and the values $E_a^D = 21.57 \pm 0.18$ kcal/mol and $\ln A^D = 28.37 \pm 0.28$ are accepted. Rates were measured at 5 °C intervals and all eleven temperatures are used for the Arrhenius calculation. By use of the −10 to 50 °C Arrhenius parameters for V-*h*, values of $\Delta E_a^{D-H} = 0.31$ kcal/mol and $A^H/A^D = 2.51$ can be calculated. On the other hand, when only rate measurements between 50 and 70 °C are used, the values change dramatically to $\Delta E_a^{D-H} = 2.6$ kcal/mol and $A^H/A^D = 0.06$.

We have always been sensitive to the possibility of curvature in an Arrhenius plot for elimination reactions that do not follow a concerted mechanism. For this reason, we often use a 50 °C temperature range and frequently measure rate constants at 5 °C intervals. In the case cited above for the reaction of V-*h* with ethanolic sodium ethoxide, the curvature in the Arrhenius plot could easily have gone undetected. Since there is a curvature in the Arrhenius plot, it is meaningless to attempt to correlate the observed k^H/k^D values with current theories of primary kinetic isotope effects.

Kinetic studies on the methanolic sodium methoxide promoted dehydrochlorination of V-*h* and V-*d* were not as extensive as those carried out in ethanol. Over the temperature ranges used for calculation of the Arrhenius parameters reported in Table II, no apparent curvature was observed.[22]

Reaction of V is further complicated since small amounts of $C_6H_5CH{=}CHCl$ are formed along with the expected $C_6H_5CCl{=}CH_2$. The rates used to calculate Arrhenius parameters reported in Table II were always corrected for "wrong way" elimination which corresponds to 0.8–1.7% for V-*h* and 5.1–6.9% for V-*d* when using ethanolic sodium ethoxide. Sodium methoxide in methanol results in about twice the amount of β-chlorostyrene from V-*h*, while only trace amounts of the "wrong way" isomer were detected when potassium *tert*-butoxide in *tert*-butyl alcohol was used. Relative rates of V measured in *t*-BuOK (*t*-BuOH):EtONa (EtOH) = 230:1.0 and EtONa (EtOH):MeONa (MeOH) = 11:1.0 are consistent with other published results from our laboratories.[12,23]

Although slightly smaller in magnitude, the chlorine isotope effects parallel those measured for III. Both the methoxide-promoted (1.00978 ± 0.00020 at 21 °C) and the ethoxide-pro-

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[18] Root, K. S.; Touchette, N. A.; Koch, J. G.; Koch, H. F. Abstracts of Papers, Euchem Conference on Mechanisms of Elimination Reactions, Assisi, Italy, September 12–16, 1977.

[19] Reference 3, Figure 1 (p 6103) and Table II (p 6104) case (d), has calculated results that would lead to this type of behavior.

[20] Values at 40 °C were not included.

[21] A minimum of two runs at each temperature was taken for a total of over 55 kinetic runs. At the higher temperatures that were crucial to the point of deviation from the slope, we made between four and six runs at each temperature. One could say we "beat this system to death".

[22] Rates obtained at 75 °C for V-*h* did show an 8% negative deviation from the line. However, we cannot at this time state whether this deviation is due to a similar curvature of the Arrhenius plot or is due to poor kinetics.

[23] (a) Koch, H. F.; Tumas, W.; Knoll, R. *J. Am. Chem. Soc.* **1981**, *103*, 5423–5429. (b) *Ibid.* 5427–5428. The argument is made for *tert*-butyl alcohol vs. ethanol, but the data cited for ethanol and methanol can lead to the conclusion of more internal return for MeOH than for EtOH.

moted (1.00908 ± 0.00008 at 24 °C) k^{35}/k^{37} values for V-*h* are close in magnitude and differ from those observed for V-*d* in methanol (1.00776 ± 0.00020 at 21 °C) or ethanol (1.00734 ± 0.00012 at 24 °C).

Our current understanding of a detailed mechanism for the alkoxide-promoted dehydrochlorination of either III or V is not sufficient to attempt modeling both hydrogen and chlorine isotope effects. Standard calculations used to model PKIE for a concerted elimination process suggest that the experimental values are inconsistent with a single-step reaction (vide infra). The treatment proposed in ref 3 ignores the possibility of a chlorine isotope effect on the proton transfer step, k_1 in Scheme I; however, the large k^{35}/k^{37} obtained for III and V can be rationalized with an internal-return mechanism. Qualitatively both hydrogen and chlorine isotope effects are consistent with an internal-return mechanism.

The hydrogen PKIE at 25 °C are smaller when reaction occurs in methanol, 2.29 (III) and 3.83 (V), than values obtained for reaction in ethanol, 2.73 (III) and 4.24 (V). These results are consistent with the suggestion that there is more internal return for methanol than for ethanol.[23b] The greater the amount of internal return, the larger the contribution of k_2 to the observed rate constant for the reaction. Therefore, $(k^{35}/k^{37})_{\mathrm{MeOH}}$ should be greater than $(k^{35}/k^{37})_{\mathrm{EtOH}}$, and this occurs with the experimental results: for III, $(k^{35}/k^{37})^{\mathrm{H}}_{\mathrm{MeOH}} = 1.01255$ (20 °C) $>$ $(k^{35}/k^{37})^{\mathrm{H}}_{\mathrm{EtOH}} = 1.01229$ (0 °C) and $(k^{35}/k^{37})^{\mathrm{D}}_{\mathrm{MeOH}} = 1.01025$ (20 °C) $>$ $(k^{35}/k^{37})^{\mathrm{D}}_{\mathrm{EtOH}} = 1.01003$ (0 °C); for V, $(k^{35}/k^{37})^{\mathrm{H}}_{\mathrm{MeOH}} = 1.00978$ (21 °C) $>$ $(k^{35}/k^{37})^{\mathrm{H}}_{\mathrm{EtOH}} = 1.00908$ (24 °C) and $(k^{35}/k^{37})^{\mathrm{D}}_{\mathrm{MeOH}} = 1.00776$ (21 °C) $>$ $(k^{35}/k^{37})^{\mathrm{D}}_{\mathrm{EtOH}} = 1.00734$ (24 °C). There is a good correlation between the magnitude of $k^{\mathrm{H}}/k^{\mathrm{D}}$ and the corresponding k^{35}/k^{37}; however, to pursue that point would be pushing the experimental results further than warranted at this time.

The differences in k^{35}/k^{37} for I-*h* and I-*d* could also be consistent with a two-step mechanism if about 1.005 of the observe value comes from a chlorine isotope effect on k_1(vide infra). The difference between I-*h* and I-*d* (ca. 1.0009) could then be attributed to k_2 with a transition state that has very little additional C–Cl bond elongation over that in the carbanion intermediate. On the basis of this analysis, we would certainly be presumptuous to suggest that the mechanism for the ethoxide-promoted dehydrochlorination of I was not E2. Kwart and Horgan[17b] have recently reported that a deactivated analogue of I; namely, $PhCHDCBr(CH_3)CO_2CH_3$ yields a temperature-independent PKIE, $k^{\mathrm{H}}/k^{\mathrm{D}} = 1.227$, and this appears to be inconsistent with a concerted pathway.

Model Calculations of Isotope Effects for E2 Transition States. Two facets of the experimental isotope effect results have no precedent, and we have therefore employed a theoretical analysis to examine the consequences more closely. We know of no other solution process for which the isotope effect upon an isotope effect has been recorded, and therefore a scale of normality needs to be developed. Furthermore, the chlorine isotope effect for III-*h* is the largest yet reported and that for V-*h* is also unusually large. Some knowledge as to what type of transition state might give rise to such results is required.

As far as the dependence of k^{35}/k^{37} upon the isotopic identify of the departing hydron in elimination reactions is concerned, we have only intuition and the result for I-Cl-*h* vs. I-Cl-*d* to convince us that $(k^{35}/k^{37})_{\mathrm{H}}$ and $(k^{35}/k^{37})_{\mathrm{D}}$ should be about the same for an E2 process. Thus, our conviction that the reported chlorine isotope effects observed from the reactions of III and V are not compatible with an E2 process is not particularly firmly based.[24] Calculations have therefore been performed, using as models a wide range of E2 transition state structures for dehydrochlorination of I-Cl-*h* and I-Cl-*d* in order to test the correctness or otherwise of our intuitive reasoning.

To conserve computer time, a cutoff structure for I-Cl and the corresponding transition states was employed.[25] The methyl group was represented by a point mass of 15 amu, the three most remote carbons of the phenyl group were deleted, and the alkoxide ion in the transition state was approximated as C-O.[26] Transition state models containing partial bonds are conveniently described in terms of bond orders for the O⋯O (n_{OH}), H⋯C_β (n_{HC}), $C_\beta \overline{\cdots} C_\alpha$ (n_{CC}) and C_α⋯Cl (n_{CCl}) partial bonds. If the earlier arbitrary restraints[26] are placed upon these bonds orders, namely $n_{\mathrm{OH}} + n_{\mathrm{HC}} = 1.0$, $n_{\mathrm{CC}} + n_{\mathrm{CCl}} = 2.0$ if $n_{\mathrm{HC}} \leq n_{\mathrm{CCl}}$ (carbanion-like transition states) or $n_{\mathrm{CC}} + n_{\mathrm{HC}} = 2.0$ if $n_{\mathrm{HC}} \geq n_{\mathrm{CCl}}$ (carbocation-like transition states), only n_{HC} and n_{CCl} are required to define the position of a model on a More O'Ferrall diagram for E2 transition states.[27]

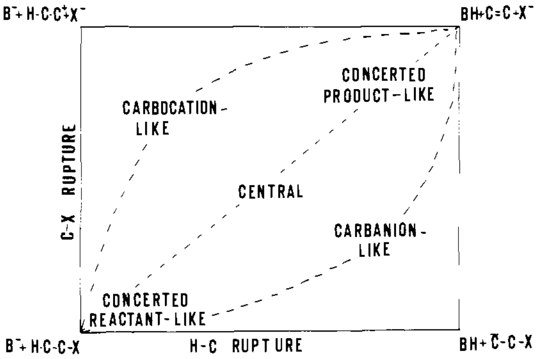

Figure 1. More O'Ferrall potential energy surface for E2 reactions. The positions of transition states are those used to calculate theoretical results shown in Table III.

The simple valence force field was that employed in previous calculations.[26] Interaction force constants required to generate the necessary reaction coordinate motion by respectively coupling the O⋯H/H⋯C, the H⋯C/C$\overline{\cdots}$C, and the C$\overline{\cdots}$C/C⋯Cl stretches were formulated in the usual way:

$$f_{ij}^{\ddagger} = a_{ij}(f_{ii}^{\ddagger} f_{jj}^{\ddagger})^{1/2}$$

where $f_{ii}^{\ddagger}$ and $f_{jj}^{\ddagger}$ are the relevant diagonal stretching force constants, with the a_{ij} coefficients being subject to the condition:[28]

$$1 - a_{12}^2 - a_{23}^2 - a_{34}^2 + a_{12}^2 a_{34}^2 = D(D \text{ negative})$$

Three combinations of coefficients were investigated. Reaction coordinate H in which protonic motion is emphasized was simulated by $a_{12} = 1.05$, $a_{23} = a_{34} = 0.3296$, $D = -0.2$. Reaction coordinate HA which emphasizes heavy atom motion at the expense of protonic motion utilized $a_{12} = 0.90$, $a_{23} = a_{34} = 0.5725$, $D = -0.2$. Finally, a reaction coordinate (HHA) which involved considerable protonic and heavy atom motion was associated with $a_{12} = 1.05$, $a_{23} = a_{34} = 0.4691$, $D = -0.3$.

Vibrational analyses and isotope effect calculations were performed by our usual program[26] which is a local variant of BEBOVIB-IV.[29] The temperature range was 100–600 K and the simple Bell tunnel correction was included. The specific isotope effects calculated for dehydrochlorination of $C_6H_5C^iH(CH_3)CH_2Cl$ were $k^{\mathrm{H}}/k^{\mathrm{D}}$ (^{i}H = H and D, respectively), k^{12}/k^{14} for C_α and C_β, and k^{35}/k^{37} for chlorine. The last three were separately calculated for ^{i}H = H and D. The results comprise a 5 × 5 × 3 array of isotope effects since n_{HC} and n_{CCl} were independently decreased from 0.9 to 0.1 in steps of 0.2, and all three reaction coordinate formulations were successively employed for each model. Factors ignored were solvation of the leaving group[30] and the possibility of transition state looseness ($n_{\mathrm{OH}} + n_{\mathrm{HC}} < 1.0$)[31] both of which

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(24) The hydrogen isotope effects for III are definitely not compatible with a concerted mechanism and current theories.

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Table III. Theoretical Results for Various Transition State Types in the Model $C_6H_5C^iH(CH_3)CH_2Cl$ Reaction at 50 °C

				$^iH = H$			$^iH = D$	
type[a]	n_{HC}	n_{CCl}	reactn coordinate	k^H/k^D	k^{35}/k^{37}	α-k^{12}/k^{14}	k^{35}/k^{37}	α-k^{12}/k^{14}
concerted reactant-like	0.7	0.7	H	5.53	1.0021	1.0052	1.0021	1.0058
	0.7	0.7	HA	3.86	1.0024	1.0300	1.0026	1.0270
	0.7	0.7	HHA	5.12	1.0021	1.0078	1.0021	1.0100
central	0.5	0.5	H	5.83	1.0035	1.0031	1.0036	1.0033
	0.5	0.5	HA	3.95	1.0042	1.0250	1.0045	1.0210
	0.5	0.5	HHA	5.46	1.0035	1.0057	1.0036	1.0068
concerted product-like	0.3	0.3	H	4.07	1.0052	1.0056	1.0053	1.0048
	0.3	0.3	HA	3.66	1.0086	1.0240	1.0089	1.0210
	0.3	0.3	HHA	4.04	1.0052	1.0098	1.0053	1.0085
carbanion-like	0.3	0.7	H	4.12	1.0023	1.0056	1.0024	1.0050
	0.3	0.7	HA	2.96	1.0039	1.0220	1.0040	1.0190
	0.3	0.7	HHA	4.07	1.0023	1.0100	1.0025	1.0095
carbocation-like	0.7	0.3	H	5.54	1.0051	1.0350	1.0051	1.0350
	0.7	0.3	HA	3.90	1.0054	1.0600	1.0056	1.0550
	0.7	0.3	HHA	5.14	1.0051	1.0360	1.0052	1.0390

[a] See Figure 1 for approximate positions.

would require further adjustable parameters.

Results are not presented in detail since the patterns that emerged are similar to those for a well-documented E2 model system.[26] In Table III we therefore show isotope effects[32] for typical transition states lying in five regions of the More O'Ferrall potential energy surface for E2 reactions (Figure 1).[27a]

The result of immediate importance is that k^{35}/k^{37} is almost independent of the isotopic identity of the β-hydrogen. Our intuitive prediction for the E2 mechanism is thus confirmed by this wide range of models. It is also noteworthy that the α-carbon isotope effect is also independent of whether ^iH = H or D. It then follows, within the range of models investigated, that any elimination for which $(k^{35}/k^{37})_H \neq (k^{35}/k^{37})_D$ is neither an E2 nor an (E1cB)$_I$, $k_2 \gg k_{-1}$, process.[33]

The calculations suggest that if anything, $(k^{35}/k^{37})_D$ should be slightly larger than $(k^{35}/k^{37})_H$ whereas the experimental trend is in the opposite direction for I-Cl-*h* and I-Cl-*d*. The Born–Oppenheimer approximation is implicit in our model calculations, in that force constants and transition state geometry for each model are assumed to be independent of isotopic mass. It is of interest to note that a recent variant of transition-state theory indicates that this may not always be the case.[34] It would be presumptuous to suggest that the present small discrepancy between theory and experiment is a manifestation of a breakdown in the Born–Oppenheimer approximation; however, such a possibility should not be ignored.

Possible Origin of Unusual High Chlorine Isotope Effects. The large chlorine isotope effect for the dehydrochlorination of III now requires comment. The above E2 models can serve for an internal-return E1cB process if transition states with $n_{OH} > n_{HC}$ are examined. The sole model that produces k^{35}/k^{37} in the vicinity of the observed values is one involving a 90% broken C–Cl bond (reaction coordinate HA). A simple Hammond postulate argument based on a hydrogen-bonded carbanion as an unstable intermediate along the reaction pathway[35] would suggest less than 50% C–Cl bond breaking in the transition state for an internal-return process of the type we have so far been considering.

There is no doubt that formulations for the interaction force constants that yield even greater amounts of heavy atom motion than model HA will lead to larger values of k^{35}/k^{37}, but trial calculations in other systems show that k^H/k^D is reduced to improbably small or even inverse values.[36] We note that large values of k^{35}/k^{37} (up to 1.025) are calculated for S_N1 models simulating the solvolysis of *t*-BuCl with $n_{CCl} = 0.8$[30] and have therefore attempted to incorporate a feature of the force constant dependence by performing calculations on I-Cl where the H-C_β and C_α–Cl bonds are not coplanar. In this model, the C_β–C_α–Cl bending force constant is not dependent on the product of n_{CC} and n_{CCl} if double-bond formation is permitted to lag behind C–Cl extension.[37] This modification unexpectedly produced even lower chlorine isotope effects and was therefore of no use.

Does the failure of the internal return mechanism to either quantitatively or qualitatively reproduce the large chlorine isotope effects disqualify it from consideration? We think not, and now consider a further factor which has hitherto escaped widespread attention.

If the carbanion in any sort of E1cB process is stabilized by orbital interaction with the potential leaving group, the consequence is a weakened C–X bond. Whatever the origin of this effect may be,[38] it follows that the proton transfer step, k_1, could also be subject to a chlorine isotope effect. We do not need to invoke hyperconjugation for our model since the argument will depend solely on the bond elongation of the leaving halogen. Rappoport et al.[39] and Ahlberg and Thibblin[40] have earlier argued for such an effect. Their proposal has been given a theoretical seal of respectability by Apeloig and Rappoport[41] who show that such stabilization is more important for X = Cl than for X = F. While we question the quantitative significance of the stabilization parameters presented by Thibblin,[42] there can be little doubt the effect is real and that it must be taken into account in the present case.

Consider an internal-return process in which all the rate constants are isotopically sensitive to chlorine mass but only k_1 and k_{-1} are sensitive to the hydrogen mass. In the following, RHCl symbolizes the substrate and R the product olefin. The following reactions need to be considered:

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(31) McLennan, D. J. *Aust. J. Chem.* **1979**, *32*, 1883–1896.

(32) The tabulated results do not incorporate the calculated tunnel corrections on the grounds that the corrections do not influence the patterns obtained.

(33) We have not tried to match theory with experiment for any particular transition-state model since the number of adjustable parameters is too great to allow this when isotope effects for only two or three atoms are available.

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(41) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095–5098.

(42) Thibblin[40d] has stabilization factors for X = Me and X = OH both equal to zero, whereas Apeloig and Rappoport[41] calculate a 9.4 kcal mol^{-1} difference in favor of OH at the STO-3G ab initio level.

$$\mathrm{B^- + RH^{35}Cl} \underset{{}^{\mathrm{H}}k_{-1}^{35}}{\overset{{}^{\mathrm{H}}k_1^{35}}{\rightleftharpoons}} \mathrm{BH\cdots\bar{R}^{35}Cl} \xrightarrow{k_2^{35}} \mathrm{BH + R + {}^{35}Cl^-}$$

$$\mathrm{B^- + RH^{37}Cl} \underset{{}^{\mathrm{H}}k_{-1}^{37}}{\overset{{}^{\mathrm{H}}k_1^{37}}{\rightleftharpoons}} \mathrm{BH\cdots\bar{R}^{37}Cl} \xrightarrow{k_2^{37}} \mathrm{BH + R + {}^{37}Cl^-}$$

$$\mathrm{B^- + RD^{35}Cl} \underset{{}^{\mathrm{D}}k_{-1}^{35}}{\overset{{}^{\mathrm{D}}k_1^{35}}{\rightleftharpoons}} \mathrm{BD\cdots\bar{R}^{35}Cl} \xrightarrow{k_2^{35}} \mathrm{BD + R + {}^{35}Cl^-}$$

$$\mathrm{B^- + RD^{37}Cl} \underset{{}^{\mathrm{D}}k_{-1}^{37}}{\overset{{}^{\mathrm{D}}k_1^{37}}{\rightleftharpoons}} \mathrm{BD\cdots\bar{R}^{37}Cl} \xrightarrow{k_2^{37}} \mathrm{BD + R + {}^{37}Cl^-}$$

The observed rate constants are of the form:

$${}^{i\mathrm{H}}k_{\mathrm{obsd}}{}^{j} = \frac{{}^{i\mathrm{H}}k_1{}^{j}k_2{}^{j}}{{}^{i\mathrm{H}}k_{-1}{}^{j} + k_2{}^{j}}$$

$${}^{i}\mathrm{H} = \mathrm{H} \text{ or } \mathrm{D},\ j = 35 \text{ or } 37 \text{ for chlorine}$$

whence

$$\frac{{}^{\mathrm{H}}k_{\mathrm{obsd}}{}^{35}}{{}^{\mathrm{H}}k_{\mathrm{obsd}}{}^{37}} = \frac{{}^{\mathrm{H}}k_1{}^{35}(a_{37}{}^{\mathrm{H}} + 1)}{{}^{\mathrm{H}}k_1{}^{37}(a_{35}{}^{\mathrm{H}} + 1)} \tag{1}$$

where $a_j{}^{i\mathrm{H}} = {}^{i\mathrm{H}}k_{-1}{}^{j}/k_2{}^{j}$ (internal return ratio). Similarly

$$\frac{{}^{\mathrm{D}}k_{\mathrm{obsd}}{}^{35}}{{}^{\mathrm{D}}k_{\mathrm{obsd}}{}^{37}} = \frac{{}^{\mathrm{D}}k_1{}^{35}(a_{37}{}^{\mathrm{D}} + 1)}{{}^{\mathrm{D}}k_1{}^{37}(a_{35}{}^{\mathrm{D}} + 1)} \tag{2}$$

We are required to show that the observed chlorine isotope effect given by eq 1 is greater than that given by eq 2. It is reasonable to assume that $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}}$ is independent of chlorine mass, and in fact this has been confirmed by the model calculations. The consequent inequality required is now

$$\frac{(a_{37}{}^{\mathrm{H}} + 1)}{(a_{35}{}^{\mathrm{H}} + 1)} > \frac{(a_{37}{}^{\mathrm{D}} + 1)}{(a_{35}{}^{\mathrm{D}} + 1)} \tag{3}$$

Let

$$a_{35}{}^{\mathrm{H}} = xa_{35}{}^{\mathrm{D}} \tag{4}$$

$$a_{37}{}^{\mathrm{H}} = xa_{37}{}^{\mathrm{D}} \tag{5}$$

and it follows that $x > 1$ is one condition for inequality 3 to hold. The other is $y > 1$, where $a_{37}{}^{\mathrm{D}} = ya_{35}{}^{\mathrm{D}}$ and $a_{37}{}^{\mathrm{H}} = ya_{35}{}^{\mathrm{H}}$. This is eminently reasonable in the chemical sense, in that it requires internal return to be more marked for the H than the D compound, which is known to be the case.[3,43] Equations 4 and 5 are likewise reasonable in that they require equality of ${}^{\mathrm{H}}k_{-1}{}^{35}/{}^{\mathrm{D}}k_{-1}{}^{35}$ and ${}^{\mathrm{H}}k_{-1}{}^{37\mathrm{D}}k_{-1}{}^{37}$. Since the equality is found to prevail for the deprotonation steps and since it is unlikely that the equilibrium hydrogen isotope effects will be sensitive to chlorine mass, these reprotonation isotope effects should be essentially equal.

Thus, a slight modification of the earlier internal return system[3] allows us to rationalize the hydrogen mass effect on the observed chlorine isotope effect and also gives an explanation as to why no single set of parameters based on the earlier treatment permits simulation of both $k^{\mathrm{H}}/k^{\mathrm{D}}$ and k^{35}/k^{37} for either of the internal-return processes considered here. The reason for the latter is that the effect of chlorine mass on ${}^{i\mathrm{H}}k_1$ does not fall within the ambit of the Koch and Dahlberg treatment.

The large chlorine isotope effects are also consistent with the above mechanism. The carbon–chlorine bond will be weakened by orbital interaction in the carbanion-forming step and will be further weakened in the k_2 step as a result of the C–Cl bond rupture. In the case of an E1cB process that features internal return, the transition state for the second step can therefore have a C–Cl bond that may be only 90% of the ground-state value since the intermediate already has a sizeable elongation. For this reason the previous argument based on the Hammond postulate may not be applicable. It is not yet possible to give a firm estimate of how much bond weakening accompanies carbanion formation with chlorine as the leaving gruop; however, an estimate of the minimum amount can be made. Ab initio calculations reveal that a carbon–fluorine bond is lengthened by 0.126 Å on going from $\mathrm{CH_3CF_3}$ to $\mathrm{(CH_2CF_3)^-}$.[44] This corresponds, in terms of the Pauling equation,[26,30] to a reduction in the bond order from 1.0 to 0.66. It should also be noted that only one of the three C–F bonds in $\mathrm{CF_3C^-H_2}$ shows this elongation. The C–F bond that is antiperiplanar to the lone pair electrons goes from 1.361 Å in $\mathrm{CF_3CH_3}$ to 1.487 Å in the carbanion, while the other two C–F bonds show only a slight elongation to 1.396 Å.[44b]

Chlorine is likely to suffer an even greater decrease in bond order,[41] so the 0.66 value calculated for the C–F bond could be regarded as the minimum value for the carbanions under consideration in our systems. Bach and Wolber[45] have carried out calculations on the addition of several nucleophiles to a series of halosubstituted ethylenes. They conclude that whenever a given structure has a choice between a C–Cl or C–F bond in the antiperiplanar position to the β-carbanion, the calculated energetics favor the C–Cl bond at all times. This could be attributed to the fact that C–Cl has a lower σ^* to interact with the lone pair electrons of the carbanion. If the proton transfer transition states resemble the carbanion, the present calculations reveal that a minimum chlorine isotope effect of between 1.005 and 1.008 can be expected. The actual value will depend upon the degree of proton transfer and the reaction coordinate formulation employed. If a further 40% extension of the C_α–Cl bond occurs in the second step, k_2, and if the chlorine isotope effect on the proton transfer step, k_{-1}, is negligible, a maximum of ca. 1.016 for the overall isotope effect in an internal-return mechanism can be estimated. Since an internal-return process with $k_{-1} \approx k_2$ could conceivably yield k^{35}/k^{37} between 1.008 and 1.016, the present results for III-h in particular are nicely accommodated.

Use of Heavy-Atom Isotope Effects and Element Effects to Distinguish between Elimination Mechanisms. In light of the above explanation for large observed chlorine isotope effects, our previous view,[46] that the study of heavy-atom isotope effects coupled with a hydrogen isotope effect on these values could distinguish between three major 1,2-elimination reaction mechanisms, must be altered. We should state that we adhere to the Jencks definition[47] that an intermediate is a species with a significant lifetime[48] that has barriers for its breakdown to both reactants and products or other intermediates. We have already discussed the case where internal return, $k_{-1} \geq k_2$ in Scheme I, plays a significant role in determining the magnitude of observed isotope effects and will now comment on the case of an $(\mathrm{E1cB})_{\mathrm{I}}$ where $k_2 \gg k_{-1}$.

Hydrogen isotope effects cannot be used to distinguish between E2 and $(\mathrm{E1cB})_{\mathrm{I}}$ pathways.[5] It has been suggested that the observation of heavy-atom isotope effects would rule out the $(\mathrm{E1cB})_{\mathrm{I}}$ path in favor of an E2 mechanism;[5] however, the postulation of a leaving group isotope effect in the proton transfer component of an E1cB process has serious consequences regarding this assumption. The same argument should apply to α-carbon isotope effects, since the bonding of C_α can also be altered by orbital interaction of the halide and carbon in a carbanion. Therefore, previous interpretations of chlorine isotope effects measured for the dehydrochlorination of $\mathrm{Ar_2CHCHCl_2}$ compounds[10] and C_α isotope effects observed for $\mathrm{Ar_2CHCCl_3}$ reactions[49] will have to be reassessed in this light, and work is currently in progress to deal with these matters.

In the absence of measuring leaving group isotope effects, Bunnett et al.[6] cleverly suggested the use of an "element effect"

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(45) Bach, R. D., private communication.

(46) Reference 3, p 6107.

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(48) A significant lifetime must be one longer than that of a molecular vibration of ca. 10^{-13} s.

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during their investigations of aromatic nucleophilic substitution reactions. We have found this to be a useful experimental probe in our studies of nucleophilic reactions of halogenated alkenes, but we have serious reservations about using element effects to aid in assigning proper mechanisms for dehydrohalogenations. The relative rates of ethoxide-promoted eliminations for I-Br vs. I-Cl are 52:1.0 at 75 °C and other experimental evidence suggests that these reactions proceed by an E2 mechanism. Two other systems reported in this study, $C_6H_5CHClCF_2Cl$ (III) and $C_6H_5CHClCH_2Cl$ (V), appear not to react via a concerted pathway, and still result in large element effects when compared to their bromine analogues $C_6H_5CHBrCF_2Br$ (II), $k^{II}/k^{III} = 49$ at 25 °C, and $C_6H_5CHBrCH_2Br$ (VI), $k^{VI}/k^{V} = 31$ at 25 °C.[16] There also appears to be no correlation between the observed chlorine isotope effects and element effects that are reported in Table I. If the effect of a β-bromine on the proton transfer step of an E1cB reaction is significantly greater than that of a β-chlorine, then the observation of element effects in E1cB reactions may be rationalized by an argument that makes use of an orbital interaction between the LUMO associated with the α-carbon/halogen bond and the HOMO bearing the carbanionic charge.

In an elegant piece of experimental work, More O'Ferrall et al.[50] recently measured kinetics for the methoxide-promoted dehydrohalogenation reactions of 9-halo-9,9′-bifluorenyls (VII-X) to form bifluorenylidene in methanol. They observe unusually small leaving group element effects of $k^{VII\text{-}Cl}/k^{VII\text{-}F} = 0.7$ and $k^{VII\text{-}Br}/k^{VII\text{-}Cl} = 1.9$. They sugegst that the formation of a carbanion is unassisted by halogen hyperconjugation (orbital interaction) even though reaction appears to occur via an $(E1cB)_I$ mechanism, $k_2 \gg k_{-1}$. The carbanion that is generated by removal of the hydrogen on the 9-position of a fluorene system will undoubtedly be a highly delocalized species.[51] If the most stable configuration of VII-X has the 9′-hydrogen and the 9-halogen in a gauche arrangement, it would seem reasonable that an orbital interaction between the developing carbanionic charge and the halogen could be minimized. Therefore, the rate-limiting step of proton transfer from carbon to oxygen could occur independent of the identity of the β-halogen. The same delocalization factor may be responsible for no chlorine isotope effect observed in the E1cB dehydrochlorination of $(p\text{-}NO_2C_6H_4)_2CHCHCl_2$, where the k_1 step is thought to be rate limiting.[10] Model calculations may clarify this point and are planned.

Baciocchi et al.[52] have observed a similar inversion in relative rates of dehydrochlorination when compared to dehydrofluorination, $k^{Cl}/k^{F} = 0.24$ at 30 °C, for syn eliminations from 1,2-dihalogenoacenaphthenes promoted by potassium *tert*-butoxide in *tert*-butyl alcohol. This system should have a minimal amount of orbital interaction between the β-halogen and the developing carbanionic charge, which can be delocalized into the naphthalene ring system. When the base/solvent pair is changed to potassium ethoxide in ethanol, loss of HCl occurs faster than does the elimination of HF, $k^{Cl}/k^{F} = 3.7$.[52] Although this value is still small for a normal E2 mechanism, the order is what one would predict for dehydrohalogenation reactions. The calculated rate ratios for reaction in *tert*-butyl alcohol (*t*-BK) compared to ethanol (EK) are very large, *t*-BK/EK = 1470 for loss of HCl and *t*-BK/EK = 22 800 for elimination of HF. We have suggested that values of such magnitude arise from an E1cB mechanism that features significantly less internal return in *tert*-butyl alcohol than in ethanol.[23]

Mechanisms of elimination reactions are a complicated area of chemistry. Results obtained from some of the standard physical organic methods used to probe these reactions can often be interpreted in different ways. The detailed mechanism of an elimination reaction can be very important in the study of the more fundamental problem of proton transfer reactions. We feel that careful kinetic studies on the Arrhenius behavior of isotope effects, and the measurement of a hydrogen isotope effect on leaving group isotope effects and on carbon isotope effects will become extremely useful in future studies.

Experimental Section

Materials. The synthesis of $C_6H_5C^{l}H(CH_3)CH_2Cl$ (I-Cl) will be reported in detail,[14] and $C_6H_5C^{l}HClCF_2Cl$ (III) is reported elsewhere.[53] All boiling points are uncorrected. Proton NMR spectra were recorded with a Varian T-60 and ^{19}F NMR spectra were run with a Varian HA-60IL spectrophotometer.

Preparation of $C_6H_5C^{l}HClCH_2Cl$ (V). Synthesis of V was achieved by chlorinating 15 g (0.14 mol) of $C_6H_5C^{l}H{=}CH_2$ dissolved in 150 mL of CCl_4. The reaction product was a mixture of ~70% $C_6H_5C^{l}HClCH_2Cl$ and ~30% $C_6H_5C^{l}HClCHCl_2$. This mixture of chlorinated compounds was purified by distillation through a spinning-band column. Fractions used in this study, bp 58 °C (0.4 torr), were >99% pure when analyzed by gas chromatography. Analysis after partial chlorination had occurred showed the presence of $C_6H_5C^{l}H{=}CHCl$ which accounted for the observed $C_6H_5C^{l}HClCHCl_2$.

Preparation of C_6H_5CDO. Benzaldehyde was converted to its dithiane derivative.[54] The recrystallized dithiane was converted to the lithium compound by treatment with butyl lithium and deuterium incorporation was achieved by the subsequent addition of D_2O.[54] The recrystallized deuterated dithiane was then cleaved with red HgO[55] to yield C_6H_5CDO, which was purified by vacuum distillation. Deuterium incorporation was always better than 98%. The C_6H_5CDO was then converted to either $C_6H_5CD{=}CF_2$[56] or $C_6H_5CD{=}CH_2$[57] by Wittig reactions.

Kinetics. Kinetics were carried out under pseudo-first-order conditions with ratios of alkoxide:substrate of better than 15:1. The procedure for kinetics runs has been described in detail in previous papers.[23,35b] Since kinetic samples were analyzed by gas chromatography, we were able to monitor product formation as well as substrate disappearance. This enabled us to constantly check the amount of "wrong way" elimination formed during the kinetic studies using $C_6H_5C^{l}HClCH_2Cl$.

Sample Preparation for Chlorine Isotope Effects. In a typical experiment, 20 mL of 0.3–0.5 N alcoholic sodium alkoxide was added to an accurately weighed sample of substrate ($(2\text{–}3) \times 10^{-3}$ mol) in a 50-mL Erlenmeyer. The Erlenmeyer was capped with a serum stopper and placed in a constant temperature bath long enough for 30–40% reaction to occur. After reaction, the alcoholic solution was added to 50 mL distilled water containing 2 mL of concentrated HNO_3. An additional 25 mL of water (in 2 portions) was used to rinse out the reaction vessel and combined with the other aqueous solution. The aqueous solution was then washed 3 times with 10 mL of hexane to extract any organic material. The combined hexane layers were washed with three 25-mL portions of 0.8 M KNO_3 which were added to the other aqueous solution. These aqueous solutions were warmed on a hot plate to ca. 50 °C prior to the addition of 5 mL of 1 M $AgNO_3$ solution. The resulting solution was allowed to stand overnight in a dark cupboard prior to filtration through a preweighed Gooch crucible. The crucible containing the AgCl precipitate was placed in an 80 °C oven for at least 12 h for drying. The weight of AgCl allowed a quantitative measure of the actual percent reaction.

The method for the conversion of AgCl to methyl chloride by a reaction with methyl iodide has been described elsewhere.[58,59] The mass spectrometric analyses were performed as previously described,[10] and the calculation of the isotope effect from measured isotopic ratios was done by using the standard formula.[59] Each compound studied was run in duplicate for each isotope for the 30% reaction and for infinity points in each alcohol studied. I-Cl was run 4 times for 30% reaction and 2 infinity points for each isotope. The resulting AgCl was also analyzed in duplicate since enough AgCl was obtained to convert two ~0.05-g samples to CH_3Cl.

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Registry No. I-Cl, 824-47-5; III, 434-44-6; V, 1074-11-9; D_2, 7782-39-0; ^{37}Cl, 13981-73-2; $C_6H_5CH{=}CH_2$, 100-42-5; $C_6H_5CH{=}CHCl$, 622-25-3; $C_6H_5CHClCHCl_2$, 1674-29-9; C_6H_5CDO, 3592-47-0; benzaldehyde, 100-52-7; 2-phenyldithiane, 5425-44-5; 2-lithium-2-phenyldithiane, 53178-41-9.

Kinetic Study for Spin-Trapping Reactions of Thiyl Radicals with Nitroso Compounds

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Abstract: The rate constants for the reactions of para-substituted benzenethiyl radicals with nitroso compounds have been determined by flash photolysis. For the benzenethiyl radical the rate constants (M^{-1} s^{-1}) decreased in the order pentamethylnitrosobenzene (3.2×10^8), nitrosobenzene (2.2×10^8), and 2-methyl-2-nitrosopropane (1.7×10^8). For each nitroso compound, the rate constants depend upon the para substituents of the benzenethiyl radicals. The Hammett plots vs. σ^+ yield a fairly good linear relationship; for pentamethylnitrosobenzene $\rho^+ = 0.68 \pm 0.02$ and for 2-methyl-2-nitrosopropane $\rho^+ = 0.80 \pm 0.02$. These ρ^+ values are interpreted both by the substituent effect on the thermodynamic stabilities of the thiyl radicals in the reactants and by the polar transition states. The solvent effects on the rate constants are quite small except for $p\text{-}NH_2C_6H_4S\cdot$ in which polar solvents reduce the rates.

The spin-trapping technique has been widely used to detect reactive free radicals.[1] It has been pointed out that this technique becomes more useful when absolute rate data for the trapping radicals are available.[2-4] Rate constants for carbon-centered radicals[3-10] and oxygen-centered radicals[2,11,12] have been estimated by competition experiments, where the absolute rate constants were obtained on the basis of the reference reaction. This method is only applicable to the reactions generating stable spin adducts. The spin adducts of the thiyl radicals with nitroso compounds are unstable and only detectable during in situ generation of the radicals;[13-15] therefore, it is necessary to follow directly the decay rates of the thiyl radicals in the presence of spin traps. We have shown in previous papers that the flash photolysis technique is very useful in determining the absolute rate constants for the reactions of the benzenethiyl radicals with vinyl monomers[16,17] and stable free radicals.[18] In this study we applied this method to the spin-trapping reactions of the benzenethiyl radicals with nitroso compounds; the substituent effects of both the reactants and the solvent effect are examined on the basis of the absolute rate constants.

Table I. a^N and $\tau_{1/2}$ Values of the Spin Adducts ($R(p\text{-}XC_6H_4S)NO\cdot$) in Benzene at 24 °C[a,b]

	nitrosobenzene[c]		2-methyl-2-nitrosopropane	
X	a^N, G	$\tau_{1/2}$, s	a^N, G	$\tau_{1/2}$, s
Br	11.53	2.6	17.03	1.4
Cl	11.56	2.8	17.13	1.1
H	11.54	0.98	16.75	0.75
$t\text{-}C_4H_9$	11.60	0.90	17.23	0.49
CH_3	11.66	0.87	17.28	0.41
OCH_3	11.91	0.62	17.94	0.23
NH_2	12.00	0.30	18.18	<0.10

[a] The a^N values were estimated from 15.50 G of di-*tert*-butyl nitroxide as standard. [b] The a^N value for the pentamethylnitrosobenzene–$p\text{-}ClC_6H_4S\cdot$ adduct is 16.13 G, and its $\tau_{1/2}$ is 0.60 s. [c] The a^H(para) = a^H(ortho) = 2.50–2.60 G and a^H(meta) = 0.95-1.00 G.

Results and Discussion

Transient Absorption Spectra. Figure 1 shows transient absorption spectra observed by the flash photodecomposition of bis(*p-tert*-butylphenyl) disulfide with the light between 350 and 450 nm. Since the spectrum immediately after flash (spectrum a) is similar to that generated from *p-tert*-butylbenzenethiol,

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