

Use of Kinetic Isotope Effects in Mechanism Studies. 5.¹ Isotope Effects and Element Effects Associated with Hydron-Transfer Steps during Alkoxide-Promoted Dehydrohalogenations

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Abstract: The Arrhenius behavior of the primary kinetic isotope effect, $(k^H/k^D)_{\text{Obs}}$ and $(k^H/k^T)_{\text{Obs}}$, associated with the methanolic sodium methoxide-promoted dehydrohalogenations of *m*-ClC₆H₄CⁱHCiCH₂Cl (**I**), *m*-CF₃C₆H₄Cⁱ-HCiCH₂Cl (**II**) and *p*-CF₃C₆H₄CⁱHCiCH₂F (**III**) has been used to calculate the internal-return parameters, $\mathbf{a} = k_{-1}/k_{\text{Elim}}^X$, in a two-step mechanism featuring a hydrogen-bonded carbanion. This carbanion partitions between returning the hydron to carbon, k_{-1} , and the loss of halide, k_{Elim}^X . Isotope effects at 25 °C for **I**, $(k^H/k^D)_{\text{Obs}} = 3.40$ and $(k^H/k^T)_{\text{Obs}} = 6.20$, and **II**, $(k^H/k^D)_{\text{Obs}} = 3.49$ and $(k^H/k^T)_{\text{Obs}} = 6.55$, result in similar values for \mathbf{a} : $\mathbf{a}^H = 0.59$, $\mathbf{a}^D = 0.13$ – 0.14 and $\mathbf{a}^T = 0.07$. Smaller values of $(k^H/k^D)_{\text{Obs}} = 2.19$ and $(k^H/k^T)_{\text{Obs}} = 3.56$ for **III** are due to more internal return [$\mathbf{a}^H = 1.9$, $\mathbf{a}^D = 0.50$, and $\mathbf{a}^T = 0.28$] associated with the dehydrofluorination reaction. Calculation of $k_1 (= k_{\text{Obs}} [\mathbf{a} + 1])$ results in similar isotope effects for hydron transfer in these reactions: **I**, $k_1^H/k_1^D = 4.74$ and $k_1^H/k_1^T = 9.20$; **II**, $k_1^H/k_1^D = 4.91$ and $k_1^H/k_1^T = 9.75$; **III**, $k_1^H/k_1^D = 4.75$ and $k_1^H/k_1^T = 9.17$. Reactions of *m*-ClC₆H₄CⁱHBrCH₂Br and *m*-ClC₆H₄CⁱHCiCH₂Br have very small amounts of internal return, $\mathbf{a}^H = 0.05$ and $\mathbf{a}^D = 0.01$, and $(k^H/k^D)_{\text{Obs}} = 4.95$ results in $k_1^H/k_1^D = 5.11$. The measured isotope effects are therefore due to differences in the amount of internal return and not in the symmetry of transition state structures for the hydron transfer, and the element effect, $(k^{\text{HBr}}/k^{\text{HCl}}) = 29$, for *m*-ClC₆H₄CHCⁱCH₂X is mainly due to the hydron-transfer step, $k_1^{\text{HBr}}/k_1^{\text{HCl}} = 19$, and not the breaking of the C–X bond. The kinetic solvent isotope effects, $k^{\text{MeOD}}/k^{\text{MeOH}} \approx 2.5$, are consistent with three methanols of solvation lost prior to the hydron-transfer step. The energetics associated with desolvation of methoxide ion are part of the measured reaction energetics of these systems.

Our interest in alkoxide-promoted dehydrohalogenation reactions began with measuring an extreme element effect, $k^{\text{HCl}}/k^{\text{HF}} > 10^5$, for the ethoxide-promoted eliminations of C₆H₅-CHCⁱCF₂X, where X = Cl or F. Kinetic studies of primary kinetic isotope effects [PKIE] and Hammett ρ values led to the suggestion that hydrogen-bonded carbanion intermediates are formed on the reaction coordinate.³ Alkoxide-promoted eliminations of C₆H₅CⁱHXCF₂X [X = Br or Cl and ⁱH = H or D] resulted in normal element effects, $k^{\text{HBr}}/k^{\text{HCl}} = 39$ – 48 , and medium sized PKIE, $k^H/k^D = 2.3$ to 4.5 . These results could be indicative of a concerted pathway; however, the Arrhenius behavior of the isotope effects is inconsistent with an E2 mechanism.⁴ This raises the question about the origin of the element effects associated with alkoxide-promoted dehydrohalogenations in general.

We became aware of the complexities of hydron transfer between carbon and oxygen⁵ while studying the formation of a

carbanion, $\{\text{C}_6\text{H}_5\text{C}(\text{CF}_3)\text{CF}_2\text{OCH}_2\text{CH}_3\}^-$, via either a nucleophilic addition of ethoxide to C₆H₅C(CF₃)=CF₂ or a proton abstraction from C₆H₅CH(CF₃)CF₂OCH₂CH₃. A mechanism featuring two carbanion intermediates was postulated to explain the hydrogen isotope effects that are associated with these reactions.^{6,7} One carbanion is stabilized by a hydrogen bond while the other one has no contact stabilization by either solvent or the counterion.

That mechanism has been a model for our studies of alkoxide-promoted dehydrohalogenations and alkoxide-catalyzed exchange reactions, Scheme 1. The extreme element effect obtained for the ethoxide-promoted eliminations of C₆H₅-CHCⁱCF₂Cl and C₆H₅CHCⁱCF₃ results from the loss of chloride occurring from a hydrogen-bonded carbanion, **HB**, while the loss of fluoride from –CF₃ requires the formation of a free carbanion, **FC**. Exchange of hydron from C₆H₅CⁱHCiCF₃ occurring 13 times faster than the loss of HF with a near unity

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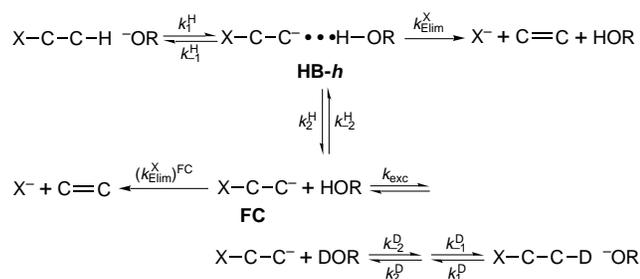
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Scheme 1

isotope effect is consistent with the loss of fluoride ion from **FC**. Since Br^- can leave from a hydrogen-bonded carbanion, $k^{\text{HBr}}/k^{\text{HCl}}$ values are normal.

Discussion and Results

Distinguishing between Concerted and Nonconcerted Alkoxide-Promoted Dehydrohalogenations. When dehydrohalogenations occur *via* the hydrogen-bonded intermediate in Scheme 1, observed rate constants are defined by

$$k_{\text{Obs}} = [k_1 k_{\text{Elim}}^{\text{X}}] / [k_{-1} + k_{\text{Elim}}^{\text{X}}] \quad (1)$$

There are two extremes: (a) $k_{-1} \gg k_{\text{Elim}}^{\text{X}}$ then $k_{\text{Obs}} = [k_1/k_{-1}] k_{\text{Elim}}^{\text{X}}$, and (b) $k_{\text{Elim}}^{\text{X}} \gg k_{-1}$ then $k_{\text{Obs}} = k_1$. For case a second-order kinetics, a near unity PKIE, and a substantial element effect are expected. Case b results in second-order kinetics, a PKIE that obeys the Swain–Schaad relationship,⁸ $k^{\text{H}}/k^{\text{D}} = (k^{\text{D}}/k^{\text{H}})^{2.26}$. For a concerted reaction, both C–H and C–X bonds are partially broken in the transition structure, and could give a variable PKIE, which obeys the Swain–Schaad relationship, as well as a variable element effect, which should be the same for the loss of HX and DX.

When neither extreme for eq 1 is applicable, all three rate constants, k_1 , k_{-1} , and $k_{\text{Elim}}^{\text{X}}$, contribute to the experimental rate constants and there is no single rate-determining step. The measured PKIE will vary between the extremes mentioned above; however, the Swain–Schaad relationship would not hold. Streitwieser *et al.* made use of deviations from the Swain–Schaad relationship and single temperature rate constants for all three hydrogen isotopes to calculate an internal-return parameter, $\mathbf{a} = k_{-1}/k_2$ [in our case $k_2 = k_{\text{Elim}}^{\text{X}}$].⁹ This parameter can be used to calculate k_1 ($= k_{\text{Obs}} [\mathbf{a} + 1]$) for all three isotopic reactions.

The use of eq 2 and a similar one for $(k^{\text{H}}/k^{\text{D}})_{\text{Obs}}$ gives an alternate way to determine the values of \mathbf{a} as well as the energetics associated with internal return by modeling experimental isotope effects obtained over a 25 to 50 °C range:¹⁰

$$\ln(k^{\text{H}}/k^{\text{D}})_{\text{Obs}} = \left[\frac{(E_1^{\text{D}} - E_{-1}^{\text{D}}) - (E_1^{\text{H}} - E_{-1}^{\text{H}})}{RT} + \ln \left(\frac{1 + (A_{\text{Elim}}^{\text{X}}/A_{-1}) \exp((E_{-1}^{\text{D}} - E_{\text{Elim}}^{\text{X}})/RT)}{1 + (A_{\text{Elim}}^{\text{X}}/A_{-1}) \exp((E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}})/RT)} \right) \right] \quad (2)$$

Three systems were used in our analysis of alkoxide-promoted dehydrohalogenations: $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{X}$ and various $\text{YC}_6\text{H}_4\text{-CHX}'\text{CH}_2\text{X}$ and $\text{YC}_6\text{H}_4\text{CHX}'\text{CF}_2\text{X}$, where X = Br, Cl, or F and X' = Br or Cl. Results from reactions of ethanolic sodium

ethoxide with all three systems are in Table 1, while those for the reactions of methanolic sodium methoxide with $\text{YC}_6\text{H}_4\text{C}'\text{-HX}'\text{CH}_2\text{X}$ and $\text{YC}_6\text{H}_4\text{C}'\text{HX}'\text{CF}_2\text{X}$ are in Table 2. The reactions of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{X}$ were previously reported,¹¹ and we measured the $k^{\text{H}}/k^{\text{D}}$ associated with $\text{C}_6\text{H}_5\text{C}'\text{H}_2\text{CH}_2\text{Cl}$ to compare it to that reported for $\text{C}_6\text{H}_5\text{C}'\text{H}_2\text{CH}_2\text{Br}$.¹² Four systems used three hydrogen isotopes to calculate internal-return parameters: *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{C}'\text{HCiCH}_2\text{Cl}$, *m*- $\text{ClC}_6\text{H}_4\text{C}'\text{HCiCH}_2\text{Cl}$, *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{C}'\text{-HCiCH}_2\text{F}$, and *m*- $\text{ClC}_6\text{H}_4\text{C}'\text{HCBRCH}_2\text{Br}$. Kinetic solvent isotope effects were measured for $\text{C}_6\text{H}_5\text{CTClCF}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{-CHClCH}_2\text{Br}$ by using mixtures of CH_3OH and CH_3OD , and the Arrhenius behavior was studied for the dehydrochlorination of *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CHClCH}_2\text{Cl}$ and the protodetritiation of *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{-CTClCF}_3$.

Hydrogen Isotope Effects Associated with the Ethoxide-Promoted Dehydrohalogenation Reactions. The results in Table 1 show a decrease in $k^{\text{H}}/k^{\text{D}}$ for ethoxide-promoted eliminations of HBr and HCl at 25 °C from the least reactive to the most reactive: $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$ (7.53), $\text{C}_6\text{H}_5\text{CHClCH}_2\text{-Br}$ (6.10), and $\text{C}_6\text{H}_5\text{CHBrCF}_2\text{Br}$ (4.51); and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl}$ (7.43), $\text{C}_6\text{H}_5\text{CHClCH}_2\text{Cl}$ (4.24), and $\text{C}_6\text{H}_5\text{CHClCF}_2\text{Cl}$ (2.73). According to theory, primary kinetic isotope effects result from differences in C–ⁱH and/or O–ⁱH bond zero-point energies in the ground state and the transition structure. Thus the Arrhenius preexponential factors, *A*, should be equal for isotopically labeled compounds,¹³ and $k^{\text{H}}/k^{\text{D}}$ results from $\Delta E_a^{\text{D-H}}$, $k^{\text{H}}/k^{\text{D}} = (A^{\text{H}}/A^{\text{D}}) \exp(\Delta E_a^{\text{D-H}}/RT)$. The single temperature PKIE values suggest a symmetrical transition structure for eliminations of $\text{C}_6\text{H}_5\text{C}'\text{H}_2\text{CH}_2\text{X}$ and later transition structures for the other eliminations.¹⁴ However, there are significant differences for the temperature dependence of the isotope effects as $A^{\text{H}}/A^{\text{D}}$ values range from 0.5 to 3.1. Arrhenius parameters associated with $\text{C}_6\text{H}_5\text{C}'\text{H}_2\text{CH}_2\text{Cl}$ are normal with $\Delta E_a^{\text{D-H}} = 1.2$ kcal/mol and $A^{\text{H}}/A^{\text{D}} = 1.1$. Although $k^{\text{H}}/k^{\text{D}}$ is the same for $\text{C}_6\text{H}_5\text{C}'\text{H}_2\text{-CH}_2\text{Br}$ (7.53), the Arrhenius parameters differ with $\Delta E_a^{\text{D-H}} = 1.6$ kcal/mol and $A^{\text{H}}/A^{\text{D}} = 0.51$, which halves the $k^{\text{H}}/k^{\text{D}}$ predicted from $\Delta E_a^{\text{D-H}}$. The latter results were interpreted as resulting from an E2 mechanism that has quantum-mechanical tunneling.¹⁵

At the other extreme are the reactions of $\text{C}_6\text{H}_5\text{C}'\text{HBrCF}_2\text{Br}$ [$\Delta E_a^{\text{D-H}} = 0.3$ kcal/mol and $A^{\text{H}}/A^{\text{D}} = 3.1$] and $\text{C}_6\text{H}_5\text{C}'\text{HCiCF}_2\text{-Cl}$ [$\Delta E_a^{\text{D-H}} = 0.1$ kcal/mol and $A^{\text{H}}/A^{\text{D}} = 2.2$], where the calculated $A^{\text{H}}/A^{\text{D}}$ accounts for 69% to 82% of the measured $k^{\text{H}}/k^{\text{D}}$. High $A^{\text{H}}/A^{\text{D}}$ values of 2.1 to 2.9 were also encountered for reactions of $\text{C}_6\text{H}_5\text{C}'\text{HCiCH}_2\text{Cl}$, *m*- $\text{ClC}_6\text{H}_4\text{C}'\text{HCiCH}_2\text{Cl}$, *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{C}'\text{HCiCH}_2\text{Cl}$, and $\text{C}_6\text{H}_5\text{C}'\text{HCiCH}_2\text{Br}$ while those obtained from reactions of *m*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}'\text{HCiCH}_2\text{Br}$,¹⁶ *m*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}'\text{HBrCH}_2\text{Br}$, and $\text{C}_6\text{H}_5\text{C}'\text{HBrCH}_2\text{Br}$ are normal with $\Delta E_a^{\text{D-H}}$ of 0.9 to 1.1, $A^{\text{H}}/A^{\text{D}}$ of 0.8 to 1.4, and $k^{\text{H}}/k^{\text{D}}$ of

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Table 1. Rate Constants, Activation Parameters, and Hydrogen Isotope Effects for Ethanolic Sodium Ethoxide-Promoted Dehydrohalogenation Reactions

compound	k , $M^{-1} s^{-1}$ (25 °C)	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu (25 °C)	k^H/k^D or k^D/k^T (25 °C)	ΔE_a , kcal	A^H/A^D or A^D/A^T	temp range, °C [no. of points]
$C_6H_5CH_2CH_2F^a$	4.35×10^{-8}	25.6	-6.4				60 to 80
$C_6H_5CH_2CH_2Cl$	2.95×10^{-6}	22.8 ± 0.1	-7.4 ± 0.2	7.43	1.2	1.1	45 to 85 [10]
$C_6H_5CD_2CH_2Cl$	3.97×10^{-7}	24.0 ± 0.3	-7.4 ± 0.6				50 to 75 [5]
$C_6H_5CH_2CH_2Br^b$	2.32×10^{-4}	20.4 ± 0.3	-6.6 ± 0.9	7.53	1.6	0.5	30 to 50 [3]
$C_6H_5CD_2CH_2Br$	3.08×10^{-5}	22.0 ± 0.2	-5.3 ± 0.5				30 to 50 [3]
$C_6H_5CH_2CF_2Cl^c$	2.47×10^{-4}	20.3 ± 0.1	-7.1 ± 0.5				25 to 70 [5]
$C_6H_5CHClCH_2F$	2.07×10^{-5}	23.1 ± 0.1	-2.4 ± 0.3	2.20	0.3	1.4	30 to 80 [12]
$C_6H_5CDClCH_2F$	9.43×10^{-6}	23.4 ± 0.1	-3.0 ± 0.3				45 to 85 [8]
$p-CF_3C_6H_4CHClCH_2F$	4.43×10^{-3}	20.4 ± 0.1	-1.0 ± 0.3	2.59	0.4	1.2	20 to 50 [6]
$p-CF_3C_6H_4CDClCH_2F$	1.71×10^{-3}	20.8 ± 0.1	-1.3 ± 0.4				20 to 50 [6]
$C_6H_5CHClCH_2Cl^{d,e}$	1.39×10^{-3}	20.7 ± 0.1	-2.3 ± 0.3	4.24	0.3	2.5	-10 to 50
$C_6H_5CDClCH_2Cl$	3.28×10^{-4}	21.0 ± 0.2	-4.1 ± 0.5				20 to 70
$m-ClC_6H_4CHClCH_2Cl$	2.64×10^{-2}	19.1 ± 0.1	-1.6 ± 0.2	4.17	0.3	2.5	-15 to 25 [17]
$m-ClC_6H_4CDClCH_2Cl$	6.33×10^{-3}	19.4 ± 0.1	-3.4 ± 0.4				10 to 50 [6]
$m-CF_3C_6H_4CHClCH_2Cl$	5.79×10^{-2}	18.8 ± 0.1	-1.3 ± 0.4	4.11	0.3	2.9	-10 to 20 [3]
$m-CF_3C_6H_4CDClCH_2Cl$	1.41×10^{-2}	19.0 ± 0.1	-3.4 ± 0.1				-10 to 40 [10]
$m-CH_3C_6H_4CHClCH_2Br$	3.06×10^{-2}	17.9 ± 0.1	-5.4 ± 0.2	5.70	1.0	1.2	-20 to 30 [11]
$m-CH_3C_6H_4CDClCH_2Br$	5.37×10^{-3}	18.9 ± 0.1	-5.7 ± 0.2				0 to 55 [10]
$C_6H_5CHClCH_2Br$	4.89×10^{-2}	18.0 ± 0.1	-4.3 ± 0.2	6.11	0.7	2.1	-10 to 25 [6]
$C_6H_5CDClCH_2Br$	8.00×10^{-3}	18.7 ± 0.1	-5.5 ± 0.5				-10 to 40 [5]
$m-CH_3C_6H_4CHBrCH_2Br^d$	2.28×10^{-2}	18.5	-3.8	5.88	0.9	1.4	-10 to 35 [10]
$m-CH_3C_6H_4CDBrCH_2Br$	3.88×10^{-3}	19.4	-4.4				0 to 50 [11]
$C_6H_5CHBrCH_2Br^d$	3.07×10^{-2}	18.1	-4.8	5.83	1.1	0.8	-20 to 30 [6]
$C_6H_5CDBrCH_2Br$	5.27×10^{-3}	19.2	-4.5				0 to 45 [6]
$C_6H_5CHClCF_3^f$	4.46×10^{-7}	29.8 ± 0.1	12.2 ± 0.2				70 to 110 [4]
$C_6H_5CHBrCF_3$	4.64×10^{-7}	29.4 ± 0.3	11.1 ± 0.9				70 to 100 [3]
$p-CF_3C_6H_4CHClCF_3$	3.84×10^{-4}	27.1 ± 0.2	16.6 ± 0.5				20 to 60 [9]
$2,6-Cl_2C_6H_3CHClCF_2Cl$	5.53×10^{-3}	17.0 ± 0.2	-11.8 ± 0.2				10 to 50 [6]
$C_6H_5CHClCF_2Cl^e$	2.21×10^{-1}	18.6 ± 0.2	0.8 ± 0.5	2.73	0.1	2.2	-20 to 15
$C_6H_5CDClCF_2Cl$	8.09×10^{-2}	18.7 ± 0.1	-0.8 ± 0.3				-15 to 25
$C_6H_5CHBrCF_2Cl$	2.14×10^{-1}	18.6 ± 0.2	0.7 ± 0.7				-25 to 15 [9]
$C_6H_5CHBrCF_2Br$	8.30	14.9 ± 0.1	-4.2 ± 0.4	4.51	0.3	3.1	-55 to -25 [8]
$C_6H_5CDBrCF_2Br$	1.84	15.2 ± 0.1	-6.5 ± 0.4				-35 to 0 [8]

^a Reference 11. ^b Reference 12. ^c Reworked data from ref 17. ^d Corrected for wrong way elimination. ^e Reference 1. ^f Reference 35.

5.70 to 5.88 at 25 °C. The solvent properties of ethanol are not as good as those for methanol, and for that reason a majority of the more detailed investigations of the $YC_6H_4C^HClCH_2X$ systems use methanolic sodium methoxide. Faster reactions in ethanolic ethoxide are attributed to less internal return for the larger ethanol.¹⁷ The k^{EtOH}/k^{MeOH} at 25 °C are 30 for $p-CF_3C_6H_4CHClCH_2F$, 11 to 17 for $YC_6H_4CHClCH_2Cl$, 10 to 11 for $YC_6H_4CHClCH_2Br$, and 7 for $C_6H_5CHBrCH_2Br$.

Comparison of the Element and Chlorine 35/37 Isotope Effects Associated with Ethoxide-Promoted Dehydrohalogenations. The element effect was first proposed by Bunnett in a 1957 paper "The 'Element Effect' as a Criterion of Mechanism in Activated Aromatic Nucleophilic Substitution Reactions",¹⁸ and has also been used for studies of dehydrohalogenation mechanisms.^{19,20} Use of k^{HBr}/k^{HCl} values replaces the measurement of chlorine isotope effects, and should result from differences of activation enthalpies for reactions with similar activation entropies. Element effects associated with

the ethoxide-promoted dehydrohalogenations of the β -phenethyl halides are good examples as $\Delta S^\ddagger = -6 \pm 1$ eu, and values of k^{HCl}/k^{HF} and k^{HBr}/k^{HCl} are due to ΔH^\ddagger differences: $k^{HCl}/k^{HF} = 68$, $\Delta\Delta H^\ddagger = 2.8$ kcal/mol [HF - HCl]; $k^{HBr}/k^{HCl} = 79$, $\Delta\Delta H^\ddagger = 3.0$ kcal/mol [HCl - HBr].

Values of k^{HBr}/k^{HCl} are similar for $C_6H_5CHClCH_2X$ (35) and $C_6H_5CHBrCF_2X$ (39); however, the k^{HCl}/k^{HF} of 67 for $C_6H_5CHClCH_2X$, which is quite normal, differs dramatically from the k^{HCl}/k^{HF} of 1.8×10^5 for $C_6H_5CHBrCF_2X$. The ΔS^\ddagger values for the $C_6H_5CHClCH_2X$ series are all within 3 eu, and the element effects are largely due to the differences in ΔH^\ddagger : $\Delta\Delta H^\ddagger = 2.4$ kcal/mol [HF - HCl] and $\Delta\Delta H^\ddagger = 2.7$ kcal/mol [HCl - HBr]. In contrast, ΔS^\ddagger values for the $C_6H_5CHBrCF_2X$ series differ significantly, favoring loss of HF [11 eu] over HCl [1 eu] and HBr [-4 eu]. The very large k^{HCl}/k^{HF} for $C_6H_5CHBrCF_2X$ comes from a much larger $\Delta\Delta H^\ddagger$ (10.8 kcal/mol) that is partially offset by a more favorable ΔS^\ddagger for the dehydrofluorination reaction. For k^{HBr}/k^{HCl} the more favorable ΔS^\ddagger for elimination of HCl from $C_6H_5CHBrCF_2Cl$ helps to compensate for the slightly larger $\Delta\Delta H^\ddagger$ of 3.7 kcal/mol (HCl - HBr).

The use of element effects to distinguish between an E2 mechanism and a multi-step process with internal return has been questioned.²¹ In Table 3 chlorine isotope effects, k^{35}/k^{37} ,

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Table 2. Rate Constants, Activation Parameters, and Hydrogen Isotope Effects for Methanolic Sodium Methoxide-Promoted Dehydrohalogenation Reactions

compd	k , $M^{-1} s^{-1}$ (25 °C)	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu (25 °C)	k^H/k^D or k^D/k^T (25 °C)	ΔE_a , kcal	A^H/A^D or A^D/A^T	temp range, °C [no. of points]
<i>p</i> -CF ₃ C ₆ H ₄ CHClCH ₂ F	1.49×10^{-4}	23.4 ± 0.1	2.6 ± 0.3	2.19	0.5	1.1	25 to 65 [10]
<i>p</i> -CF ₃ C ₆ H ₄ CDClCH ₂ F	6.81×10^{-5}	23.9 ± 0.1	2.5 ± 0.3	1.63	0.3	0.93	25 to 60 [6]
<i>p</i> -CF ₃ C ₆ H ₄ CTClCH ₂ F	4.19×10^{-5}	24.2 ± 0.2	2.6 ± 0.6				35 to 63 [9]
C ₆ H ₅ CHClCH ₂ Cl ^a	1.25×10^{-4}	21.7	-3.5			0.95	25 to 70
C ₆ H ₅ CDClCH ₂ Cl	3.26×10^{-5}	22.6	-3.4	3.83	0.9		30 to 75
<i>m</i> -ClC ₆ H ₄ CHClCH ₂ Cl	1.60×10^{-3}	21.1 ± 0.1	-0.5 ± 0.1			0.96	0 to 50 [22]
<i>m</i> -ClC ₆ H ₄ CDClCH ₂ Cl	4.71×10^{-4}	21.9 ± 0.1	-0.4 ± 0.5	3.40	0.8	0.96	10 to 60 [9]
<i>m</i> -ClC ₆ H ₄ CTClCH ₂ Cl	2.58×10^{-4}	22.3 ± 0.2	-0.0 ± 0.5	1.83	0.4	0.81	10 to 40 [3]
<i>m</i> -CF ₃ C ₆ H ₄ CHClCH ₂ Cl	3.34×10^{-3}	20.3 ± 0.1	-1.7 ± 0.2		0.8	1.0	5 to 50 [9]
<i>m</i> -CF ₃ C ₆ H ₄ CDClCH ₂ Cl	9.58×10^{-4}	21.1 ± 0.1	-1.7 ± 0.2	3.49	0.8	1.0	10 to 60 [11]
<i>m</i> -CF ₃ C ₆ H ₄ CTClCH ₂ Cl	5.10×10^{-4}	21.5 ± 0.1	-1.5 ± 0.3	1.88	0.4	0.92	20 to 55 [8]
<i>p</i> -CF ₃ C ₆ H ₄ CHClCH ₂ Cl	8.03×10^{-3}	20.08 ± 0.04	-0.7 ± 0.2				0 to 40 [7]
CH ₃ ONa/CH ₃ OD	1.98×10^{-2}	19.34 ± 0.06	-1.5 ± 0.2				0 to 35 [6]
<i>m</i> -CH ₃ C ₆ H ₄ CHClCH ₂ Br	3.12×10^{-3}	20.1 ± 0.1	-2.5 ± 0.2			1.2	5 to 55 [10]
<i>m</i> -CH ₃ C ₆ H ₄ CDClCH ₂ Br	6.23×10^{-4}	21.0 ± 0.2	-2.8 ± 0.6	5.01	0.9		20 to 70 [9]
C ₆ H ₅ CHClCH ₂ Br	4.38×10^{-3}	19.3 ± 0.1	-4.6 ± 0.2			0.67	0 to 50 [12]
C ₆ H ₅ CDClCH ₂ Br	8.07×10^{-4}	20.5 ± 0.1	-3.8 ± 0.2	5.43	1.2		5 to 60 [11]
<i>p</i> -ClC ₆ H ₄ CHClCH ₂ Br	2.35×10^{-2}	18.6 ± 0.1	-3.4 ± 0.4			0.98	-10 to 40 [7]
<i>p</i> -ClC ₆ H ₄ CDClCH ₂ Br	4.51×10^{-3}	19.6 ± 0.1	-3.4 ± 0.4	5.21	1.0		0 to 50 [11]
<i>m</i> -ClC ₆ H ₄ CHClCH ₂ Br	4.58×10^{-2}	17.8 ± 0.1	-5.0 ± 0.3			0.87	-10 to 25 [6]
<i>m</i> -ClC ₆ H ₄ CDClCH ₂ Br	9.28×10^{-3}	18.8 ± 0.1	-4.7 ± 0.3	4.94	1.0		0 to 40 [6]
<i>p</i> -CF ₃ C ₆ H ₄ CHClCH ₂ Br	1.79×10^{-1}	17.6 ± 0.1	-3.1 ± 0.2			0.91	-25 to 20 [8]
<i>p</i> -CF ₃ C ₆ H ₄ CDClCH ₂ Br	3.34×10^{-2}	18.6 ± 0.1	-2.9 ± 0.3	5.39	1.0		-15 to 30 [8]
C ₆ H ₅ CHBrCH ₂ Br	3.16×10^{-3}	19.9	-3.3			0.91	0 to 50 [6]
C ₆ H ₅ CDBrCH ₂ Br	6.00×10^{-4}	20.9	-3.2	5.27	1.0		15 to 50 [6]
<i>m</i> -ClC ₆ H ₄ CHBrCH ₂ Br	3.27×10^{-2}	18.6	-2.8			0.90	-20 to 25 [8]
<i>m</i> -ClC ₆ H ₄ CDBrCH ₂ Br	6.60×10^{-3}	19.6	-2.6	4.95	1.0		0 to 40 [8]
<i>m</i> -ClC ₆ H ₄ CTBrCH ₂ Br	3.27×10^{-3}	20.0 ± 0.1	-2.8 ± 0.4	2.02	0.4	1.1	20 to 45 [6]
<i>p</i> -CF ₃ C ₆ H ₄ CHClCF ₃	1.06×10^{-5}	27.9 ± 0.1	12.3 ± 0.3				45 to 70 [7]
<i>p</i> -CF ₃ C ₆ H ₄ CTClCF ₃ ^b	7.91×10^{-4}	25.42 ± 0.08	12.5 ± 0.3				20 to 55 [8]
CH ₃ ONa/CH ₃ OD	2.06×10^{-3}	24.86 ± 0.13	12.5 ± 0.4				20 to 45 [6]
C ₆ H ₅ CHClCF ₂ Cl	1.73×10^{-2}	20.2 ± 0.1	1.2 ± 0.3			2.3	-5 to 45 [14]
C ₆ H ₅ CDClCF ₂ Cl	7.60×10^{-3}	20.2 ± 0.1	-0.4 ± 0.3	2.28	0.0	4.7	0 to 50 [13]
C ₆ H ₅ CTClCF ₂ Cl	4.91×10^{-3}	19.6 ± 0.1	-3.5 ± 0.3	1.55	-0.6		0 to 40 [5]
C ₆ H ₅ CHBrCF ₂ Br	8.19×10^{-1}	16.7 ± 0.1	-3.0 ± 0.2			1.6	-40 to -5 [9]
C ₆ H ₅ CDBrCF ₂ Br	2.23×10^{-1}	17.0 ± 0.1	-4.6 ± 0.3	3.67	0.3		-50 to 20 [19]
C ₆ H ₅ CTBrCF ₂ Br	1.27×10^{-1}	17.1 ± 0.1	-5.1 ± 0.3	1.76	0.1	1.3	-30 to 25 [10]

^a Reference 1. ^b Kinetics are for methoxide protodetrification.

Table 3. Chlorine and Hydrogen Isotope Effects and Element Effects Associated with Alcoholic Sodium Alkoxide-Promoted Dehydrochlorination Reactions^a

compd	solvent	k^{35}/k^{37} [°C]	k^H/k^D [°C]	k^{HBr}/k^{HCl} [°C]
C ₆ H ₅ CH(CH ₃)CH ₂ Cl	EtOH	1.00590 ± 0.00013 [75]	5.37 [75]	52 [75]
C ₆ H ₅ CD(CH ₃)CH ₂ Cl		1.00507 ± 0.00036 [75]		55 [75]
C ₆ H ₅ CH ₂ CH ₂ Cl	EtOH	1.00580 ± 0.00034 [75]		
C ₆ H ₅ CHClCH ₂ Cl	EtOH	1.00908 ± 0.00008 [24]	4.24 [25]	35 [25]
C ₆ H ₅ CDClCH ₂ Cl		1.00734 ± 0.00012 [24]		24 [25]
C ₆ H ₅ CHClCH ₂ Cl	MeOH	1.00978 ± 0.00020 [21]	3.83 [25]	35 [25]
C ₆ H ₅ CDClCH ₂ Cl		1.00776 ± 0.00020 [21]		25 [25]
C ₆ H ₅ CHClCF ₂ Cl	EtOH	1.01229 ± 0.00047 [0]	2.77 [0]	66 [0]
C ₆ H ₅ CDClCF ₂ Cl		1.01003 ± 0.00024 [0]		39 [0]
C ₆ H ₅ CHClCF ₂ Cl	MeOH	1.01255 ± 0.00048 [20]	2.28 [25]	47 [25]
C ₆ H ₅ CDClCF ₂ Cl		1.01025 ± 0.00043 [20]		29 [25]

^a Data from ref 1.

are compared with k^{HBr}/k^{HCl} values for the corresponding eliminations with use of CH₃CH₂ONa/CH₃CH₂OH and CH₃ONa/CH₃OH. There is no correlation between the magnitude of k^{35}/k^{37} and k^{HBr}/k^{HCl} . If these eliminations occur by a concerted mechanism, the chlorine isotope effects should be

the same for loss of HCl or DCl; however, the amount of internal return is different for protium compared to deuterium and this results in $(k^{35}/k^{37})^{HCl} \neq (k^{35}/k^{37})^{DCl}$ for C₆H₅CⁱHClCH₂Cl and C₆H₅CⁱHClCF₂Cl.

If the breaking of a C-X bond is not the only reason for the element effect, the ability of β-halide to enhance the hydron-

Table 4. Modeling the Arrhenius Behavior of the Primary Kinetic Isotope Effects Associated with Methanolic Methoxide Promoted Dehydrohalogenation Reactions Based on Eq 2

temp, °C	$k_{\text{Obs}}^{\text{H}}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{Obs}}^{\text{D}}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{Obs}}^{\text{T}}, \text{M}^{-1} \text{s}^{-1}$	$(k^{\text{H}}/k^{\text{D}})_{\text{obs}}$	$(k^{\text{H}}/k^{\text{D}})_{\text{cal}}$	$(k^{\text{H}}/k^{\text{T}})_{\text{obs}}$	$(k^{\text{H}}/k^{\text{T}})_{\text{cal}}$	\mathbf{a}^{H}	\mathbf{a}^{D}	\mathbf{a}^{T}
<i>m</i> -ClC ₆ H ₄ C ⁱ HClCH ₂ Cl ($E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 8.75$; $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = -100$ cal/mol; $A_2/A_1 = 2.0$)										
0	5.60×10^{-5}	1.47×10^{-5}	7.46×10^{-6}	3.81	3.82	7.51	7.46	0.60	0.12	0.060
25	1.60×10^{-3}	4.71×10^{-4}	2.58×10^{-4}	3.40	3.37	6.20	6.19	0.59	0.14	0.072
50	2.73×10^{-2}	8.84×10^{-3}	5.15×10^{-3}	3.09	3.04	5.30	5.29	0.58	0.15	0.084
<i>m</i> -CF ₃ C ₆ H ₄ C ⁱ HClCH ₂ Cl ($E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 900$; $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = -100$ cal/mol; $A_2/A_1 = 2.0$)										
0	1.32×10^{-4}	3.37×10^{-5}	1.68×10^{-5}	3.92	3.98	7.86	7.93	0.60	0.11	0.056
25	3.34×10^{-3}	9.58×10^{-4}	5.10×10^{-4}	3.49	3.50	6.55	6.55	0.59	0.13	0.068
50	5.13×10^{-2}	1.62×10^{-2}	9.12×10^{-3}	3.17	3.15	5.63	5.57	0.58	0.14	0.079
<i>p</i> -CF ₃ C ₆ H ₄ C ⁱ HClCH ₂ F ($E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 850$; $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = -850$ cal/mol; $A_2/A_1 = 2.0$ [uses tritium data])										
25	1.49×10^{-4}	6.73×10^{-5}	4.22×10^{-5}	2.21	2.20	3.53	3.55	2.1	0.50	0.27
50	3.44×10^{-3}	1.64×10^{-3}	1.05×10^{-3}	2.10	2.10	3.31	3.27	1.9	0.50	0.28
75	5.06×10^{-2}	2.54×10^{-2}	1.63×10^{-2}	1.99	2.02	3.10	3.04	1.7	0.50	0.30
<i>m</i> -ClC ₆ H ₅ C ⁱ HBrCH ₂ Br ($E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 925$; $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = 1425$ cal/mol; $A_2/A_1 = 2.0$ [uses tritium data])										
0	1.68×10^{-3}	2.89×10^{-4}	1.36×10^{-4}	5.81	5.81	12.4	12.4	0.036	0.0066	0.0032
25	3.26×10^{-2}	6.60×10^{-3}	3.27×10^{-3}	4.94	4.97	9.97	9.97	0.045	0.0095	0.0049
50	4.03×10^{-1}	9.27×10^{-2}	4.82×10^{-2}	4.35	4.36	8.36	8.26	0.054	0.013	0.0070

transfer step must play a partial role. To obtain the effect of β -halide on hydron transfer, kinetics using all three hydrogen isotopes are needed to calculate the amount of internal return, $\mathbf{a} = k_{-1}/k_{\text{Elim}}^{\text{X}}$, which can be used to obtain a value for the hydron-transfer step, $k_1 = k_{\text{Obs}}[\mathbf{a} + 1]$.

Internal Return Associated with the Hydron-Transfer Step in Methoxide-Promoted Dehydrohalogenation Reactions.

When dehydrohalogenations occur by Scheme 1, the use of eq 2 and one for $(k^{\text{H}}/k^{\text{T}})_{\text{Obs}}$ allows the calculation of \mathbf{a} values as well as the energetics associated with internal return by modeling experimental isotope effects obtained over a 25 to 50 °C range.¹⁰ For example, the methanolic sodium methoxide-promoted eliminations of HCl and DCl from *m*-ClC₆H₄Cⁱ-HClCH₂Cl were studied over a 50 °C range and resulted in $k^{\text{H}}/k^{\text{D}} = 3.40$ (25 °C) with a $\Delta E_{\text{a}} = 0.8$ kcal/mol and $A^{\text{H}}/A^{\text{D}} = 0.96$, Table 2. Although the tritium kinetics were only carried out at three temperatures between 10 and 40 °C, calculated deviations for ΔH^{\ddagger} and ΔS^{\ddagger} were similar to those obtained from the deuterium data. Values of $k^{\text{H}}/k^{\text{D}}$ and $k^{\text{H}}/k^{\text{T}}$ at 0, 25, and 50 °C are obtained from the Arrhenius analyses. With use of a set value for $A_{\text{Elim}}^{\text{X}}/A_{-1}$ and starting values for $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ and $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$,²² a program will systematically change the energy terms to give the best fit for the $k^{\text{H}}/k^{\text{D}}$ data, and calculate the corresponding $k^{\text{H}}/k^{\text{T}}$. The process is repeated for a best fit for $k^{\text{H}}/k^{\text{T}}$ and calculation of the corresponding $k^{\text{H}}/k^{\text{D}}$ values.²³ With $A_{\text{Elim}}^{\text{X}}/A_{-1}$ set at a new value, the process can be repeated.

With use of the data for *m*-ClC₆H₄CⁱHClCH₂Cl and $A_{\text{Elim}}^{\text{X}}/A_{-1} = 1.0$, calculated $k^{\text{H}}/k^{\text{D}}$ values are within 0.5% of the experimental values; however, corresponding $k^{\text{H}}/k^{\text{T}}$ values are 24–29% high. The best fit for $k^{\text{H}}/k^{\text{T}}$ (–0.4 to –1.3%) gives $k^{\text{H}}/k^{\text{D}}$ values that are low by 8 to 8.4%. When $A_{\text{Elim}}^{\text{X}}/A_{-1}$ is changed to 2.0, a best fit for the $k^{\text{H}}/k^{\text{D}}$ (–0.3 to +0.6%) still has $k^{\text{H}}/k^{\text{T}}$ values that are high by 8.7 to 10.2%. However, the $k^{\text{H}}/k^{\text{T}}$ fit (–0.2 to –0.7%) gives $k^{\text{H}}/k^{\text{D}}$ values within +0.3 to –1.6% of the experimental ones, and results in $E_{-1}^{\text{D}} - E_{-1}^{\text{H}} =$

875 cal/mol,²⁴ $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = -100$ cal/mol, and internal-return parameters of $\mathbf{a}^{\text{H}} = 0.59$, $\mathbf{a}^{\text{D}} = 0.14$, and $\mathbf{a}^{\text{T}} = 0.072$ at 25 °C. If $A_{\text{Elim}}^{\text{X}}/A_{-1}$ is set at 3.0, the best fit is the same for the $k^{\text{H}}/k^{\text{D}}$ or $k^{\text{H}}/k^{\text{T}}$ data, with $k^{\text{H}}/k^{\text{D}}$ values that are within 0 to –0.3% and $k^{\text{H}}/k^{\text{T}}$ values within –1.1 to +1.5. The value for $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ is 875 cal/mol and that for $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$ is –325 cal/mol, with $\mathbf{a}^{\text{H}} = 0.58$, $\mathbf{a}^{\text{D}} = 0.13$, and $\mathbf{a}^{\text{T}} = 0.070$ at 25 °C. Since $A_{\text{Elim}}^{\text{X}}/A_{-1}$ favors elimination more in the latter case, the $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$ favors the return by an additional 225 cal/mol; however, the amounts of internal return are virtually the same for both cases. We use $A_{\text{Elim}}^{\text{X}}/A_{-1}$ values of 2.0 for the rest of our calculations.²⁵

Although the value of $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ seems low, a similar result is obtained for *m*-CF₃C₆H₄CⁱHClCH₂Cl with $A_{\text{Elim}}^{\text{X}}/A_{-1} = 2.0$: $E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 900$ cal/mol, $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = -100$ cal/mol, $k^{\text{H}}/k^{\text{D}}$ within –0.6 to +1.5%, $k^{\text{H}}/k^{\text{T}}$ within +0.9 to –0.6%, $\mathbf{a}^{\text{H}} = 0.59$, $\mathbf{a}^{\text{D}} = 0.13$, and $\mathbf{a}^{\text{T}} = 0.068$. The data are given for *m*-CF₃C₆H₄-CⁱHClCH₂Cl at nine temperatures between 5.0 and 50 °C, for *m*-CF₃C₆H₄CⁱClCH₂Cl at ten temperatures between 15 and 60 °C, and for *m*-CF₃C₆H₄CⁱClCH₂Cl at eight temperatures between 20 and 55 °C. Using the seven common temperatures for all three compounds at 5 °C intervals between 20 and 50 °C gives the same results.

A study with *p*-CF₃C₆H₄CⁱHClCH₂F at six common temperatures between 35 and 60 °C with $A_{\text{Elim}}^{\text{X}}/A_{-1}$ set at 2.0 results in a similar value for $E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 850$ cal/mol but a higher value for $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = -850$ cal/mol. The $k^{\text{H}}/k^{\text{D}}$ values are within –0.5 to +1.0% and $k^{\text{H}}/k^{\text{T}}$ are within –0.3 to –1.2%, with $\mathbf{a}^{\text{H}} = 1.9$, $\mathbf{a}^{\text{D}} = 0.50$, and $\mathbf{a}^{\text{T}} = 0.28$ at 35 °C. The larger $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$ is consistent with stronger C–F than C–Cl bonds. Since the $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ for the three systems are within 50 cal/mol, hydron transfer in the transition structures should be similar for the elimination of hydrogen chloride and hydrogen fluoride.²⁶ The lower isotope effect is usually attributed to the poorer leaving group having a later transition structure. For our three

(24) The value of $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ is always 46 cal/mol [$\Delta H_{\text{f}}^{\text{D}} - \Delta H_{\text{f}}^{\text{H}}$] larger than $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$. Other values for the equilibrium isotope effects are as follows: $\Delta H_{\text{f}}^{\text{T}} - \Delta H_{\text{f}}^{\text{D}} = 20$ cal/mol and $\Delta H_{\text{f}}^{\text{T}} - \Delta H_{\text{f}}^{\text{H}} = 66$ cal/mol.

(25) Although the best fit is the same when based on either the $k^{\text{H}}/k^{\text{D}}$ or $k^{\text{H}}/k^{\text{T}}$ data for $A_{\text{Elim}}^{\text{X}}/A_{-1} = 3.0$, the overall fit with $k^{\text{H}}/k^{\text{T}}$ data with $A_{\text{Elim}}^{\text{X}}/A_{-1} = 2.0$ is better.

(26) When the observed rate constants are corrected for internal return, the isotope effects associated with the proton transfer step, k_1 , are within 7% at 25 °C: *m*-ClC₆H₄CⁱHClCH₂Cl, $k^{\text{H}}/k^{\text{D}} = 4.73$; *m*-CF₃C₆H₄CⁱHClCH₂-Cl, $k^{\text{H}}/k^{\text{D}} = 4.92$; *p*-CF₃C₆H₄CⁱHClCH₂F, $k^{\text{H}}/k^{\text{D}} = 4.57$.

(22) The starting point for $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ is normally 1300 cal/mol. For loss of HF and HCl the starting point for $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$ is 500 cal/mol and for loss of HBr 1800 cal/mol.

(23) We thank Duncan McLennan, Auckland University in New Zealand, for a copy of his program that models the Arrhenius behavior of primary kinetic isotope effects for a reaction that features an internal-return mechanism. The program makes use of eq 2 and a similar one for protium and tritium. The original program, in Fortran, was converted to Turbo Pascal for use with a PC, and can be obtained from J. G. Koch.

systems, the lower experimental PKIE is due to greater amounts of internal return for the dehydrofluorination than for the elimination of hydrogen chloride.

Calculations in the $\text{YC}_6\text{H}_4\text{C}^i\text{HClCH}_2\text{Br}$ systems have been hampered due to the unsuccessful syntheses of pure $\text{YC}_6\text{H}_4\text{-CTClCH}_2\text{Br}$. The use of the corresponding dibromides, $\text{YC}_6\text{H}_4\text{C}^i\text{-HBrCH}_2\text{Br}$, also presented experimental problems because of a competing wrong way elimination that forms $\text{YC}_6\text{H}_4\text{C}^i\text{H=CHBr}$.²⁷ The reaction of $m\text{-ClC}_6\text{H}_4\text{C}^i\text{HBrCH}_2\text{Br}$ resulted in less than 1% of $m\text{-ClC}_6\text{H}_4\text{CH=CHBr}$, but that increases to 3 to 6% for $m\text{-ClC}_6\text{H}_4\text{CD=CHBr}$. Therefore the tritium kinetics could result in 6% to 12% of $m\text{-ClC}_6\text{H}_4\text{CT=CHBr}$ constantly being formed, and require special treatment of the experimental data for $m\text{-ClC}_6\text{H}_4\text{CTBrCH}_2\text{Br}$.

Kinetic samples for protium and deuterium compounds are analyzed by using gas chromatography with an internal standard. Experimental rate constants at eight temperatures, -20 to 25 °C, result in a good Arrhenius plot for $m\text{-ClC}_6\text{H}_4\text{CHBrCH}_2\text{Br}$ with $E_a^{\text{H}} = 19.26 \pm 0.03$ kcal/mol that shows little change when the rate constants are corrected for wrong way elimination. However, the E_a^{D} of 20.35 ± 0.05 kcal/mol obtained from the experimental rates for $m\text{-ClC}_6\text{H}_4\text{CDBrCH}_2\text{Br}$ decreases slightly to $E_a^{\text{D}} = 20.24$ kcal/mol when corrected for the formation of $m\text{-ClC}_6\text{H}_4\text{CD=CHBr}$. This results in a ΔE_a of 1.0 instead of 1.1 kcal/mol with $A^{\text{H}}/A^{\text{D}}$ increasing from 0.76 to 0.90. Kinetic samples from the reaction of $m\text{-ClC}_6\text{H}_4\text{CTBrCH}_2\text{Br}$ will have a growing infinity point due to the formation of $m\text{-ClC}_6\text{H}_4\text{-CT=CHBr}$ in competition with $m\text{-ClC}_6\text{H}_4\text{CBr=CH}_2$. Therefore the experimental counts had to be corrected for the formation of $m\text{-ClC}_6\text{H}_4\text{CT=CHBr}$ using the rate data for the formation of $m\text{-ClC}_6\text{H}_4\text{CD=CBr}$ from $m\text{-ClC}_6\text{H}_4\text{CDBrCH}_2\text{Br}$. The corrected rate constants gave a six point Arrhenius plot over a 25 °C range [20 to 45 °C] that resulted in $E_a^{\text{T}} = 20.6 \pm 0.1$ kcal/mol and $A^{\text{T}} = 4.155 \times 10^{12}$.

Rate constants from the Arrhenius analyses are used to calculate $k^{\text{H}}/k^{\text{D}}$ and $k^{\text{H}}/k^{\text{T}}$ at 0 , 25 , and 50 °C. With $A_{\text{Elim}}^{\text{X}}/A_{-1}$ set at 2.0, values for $E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 925$ cal/mol and $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = 1425$ cal/mol are calculated for the best fit of the experimental results.²⁸ Calculated $k^{\text{H}}/k^{\text{D}}$ values are within 0.0 to +0.4%, $k^{\text{H}}/k^{\text{T}}$ are within 0.0 to -1.2% , and internal-return parameters are $\mathbf{a}^{\text{H}} = 0.045$, $\mathbf{a}^{\text{D}} = 0.0095$ and $\mathbf{a}^{\text{T}} = 0.0049$ at 25 °C. In the absence of tritium data, the Arrhenius behavior of $m\text{-ClC}_6\text{H}_4\text{CHClCH}_2\text{Br}$ and $m\text{-ClC}_6\text{H}_4\text{CDClCH}_2\text{Br}$ gives a good fit, using eq 2 with $A_{\text{Elim}}^{\text{X}}/A_{-1} = 2.0$, $E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 925$ cal/mol, $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}} = 1350$ cal/mol, $\mathbf{a}^{\text{H}} = 0.05$ and $\mathbf{a}^{\text{D}} = 0.01$.²⁹ The experimental $k^{\text{H}}/k^{\text{D}}$ values at 25 °C for the two systems are 4.95 and 4.94.

The experimental element effects, $k^{\text{Br}}/k^{\text{Cl}}$, associated with the methoxide-promoted dehydrohalogenations of $m\text{-ClC}_6\text{H}_4\text{C}^i\text{-HClCH}_2\text{X}$ can now be corrected for internal return. The $(k^{\text{HBr}}/k^{\text{HCl}})_{\text{exp}}$ of 29 results in an element effect for the proton-transfer step of $k_1^{\text{HBr}}/k_1^{\text{HCl}} = 19$, while $(k^{\text{DBr}}/k^{\text{DCl}})_{\text{exp}}$ of 20 is reduced

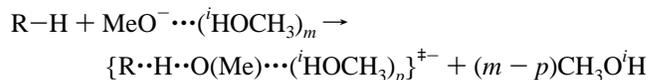
(27) A similar problem was encountered with $\text{C}_6\text{H}_5\text{CTClCH}_2\text{Cl}$ where the competitive formation of $\text{C}_6\text{H}_5\text{CT=CHCl}$ interfered with measurement of good tritium kinetics; however, $m\text{-ClC}_6\text{H}_4\text{C}^i\text{HClCH}_2\text{Cl}$ gave negligible amounts of $m\text{-ClC}_6\text{H}_4\text{CT=CHCl}$ and resulted in good kinetics.

(28) The starting point for $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$ is 1800 cal/mol for the dehydrobrominations. With A_2/A_{-1} ranging from 1.5 to 3.0, $E_{-1}^{\text{D}} - E_{-1}^{\text{H}}$ values are from 925 and 950 cal/mol, $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{X}}$ values are from 1200 and 1500 cal/mol, and internal-return parameters at 25 °C are $\mathbf{a}^{\text{H}} = 0.046 \pm 0.003$, $\mathbf{a}^{\text{D}} = 0.0097 \pm 0.008$, and $\mathbf{a}^{\text{T}} = 0.0049 \pm 0.0003$.

(29) Using only eq 2 and the temperature dependence of $k^{\text{H}}/k^{\text{D}}$ will give good modeling of the experimental results with a much larger range of $A_{\text{Elim}}^{\text{X}}/A_{-1}$ values. Since the measurement of tritium rates is not always convenient, the temptation to use only hydrogen and deuterium data must be suppressed until a consistent value of $A_{\text{Elim}}^{\text{X}}/A_{-1}$ is found for several similar systems.

slightly to $k_1^{\text{DBr}}/k_1^{\text{DCl}} = 18$. Therefore the major part of the element effect associated with this dehydrohalogenation is due to a β -bromide enhancing the hydron-transfer step, k_1 , more than a β -chloride.³⁰

Kinetic Solvent Isotope Effects [KSIE]. It has been proposed that KSIE are due to differences in the number of $\text{CH}_3\text{O}^{\text{H}}$ solvating methoxide ion and those solvating the transition structure.³¹



A fractionation factor, $\phi_{\text{OMe}} \approx 0.74$,³² for CH_3OD implies the equilibrium abundance of deuterium in the m hydrogens of a solvated MeO^- is ca. 0.74 times that in the bulk solvent. The value of m is taken as 3 which has methanol at all three possible ligand sites. At least one methanol must be lost to form the encounter complex, $\text{R-H}\cdots\text{O}(\text{Me})\cdots(\text{HOCH}_3)_p$, prior to proton transfer. Calculation of the KSIE by eq 3 determines the minimum effect, $k^{\text{OD}}/k^{\text{OH}} \approx 1.3$, when a single methanol is released to solvent ($\phi \approx 1.0$) and the transition structure fractionation factors equal those for methoxide, $\phi_{\ddagger} = \phi_{\text{OMe}}$. A maximum effect has all three methanols released to solvent and results in $k^{\text{OD}}/k^{\text{OH}} \approx 2.5$.

$$k^{\text{OD}}/k^{\text{OH}} = (\phi_{\ddagger})^p / (\phi_{\text{OMe}})^m \quad (3)$$

Reactions of $\text{C}_6\text{H}_5\text{CTClCF}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{CHClCH}_2\text{Br}$ are 2.5 times faster in pure CH_3OD than in CH_3OH . A complete study of KSIE should include kinetic runs in mixtures of CH_3OD and CH_3OH as well as in the pure solvents. Equation 4, where n is the mole fraction of CH_3OD , allows calculation of predicted rate enhancement for these mixtures:

$$k_a^{\text{OD}}/k_a^{\text{OH}} = 1/[1 - n + 0.74n]^3 \quad (4)$$

The experimental values at 25 °C for the two systems are within 4% of those predicted by eq 4: [$k_n^{\text{OD}} \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, (n)] $\text{C}_6\text{H}_5\text{CTClCF}_2\text{Cl}$, 12.3 (1.0), 8.59 (0.67), 7.31 (0.50), 6.44 (0.33), and 4.91 (0.0); $\text{C}_6\text{H}_5\text{CHClCH}_2\text{Br}$, 11.0 (1.0), 8.09 (0.75), 6.67 (0.50), 5.54 (0.25), and 4.38 (0.0).

The temperature dependence of the KSIE for methanol was also measured for the dehydrochlorination of $p\text{-CF}_3\text{C}_6\text{H}_4\text{-CHClCH}_2\text{Cl}$ and the hydrodetritiation reaction of $p\text{-CF}_3\text{C}_6\text{H}_4\text{-CTClCF}_3$. Values of $k^{\text{OD}}/k^{\text{OH}}$ are 2.76 [0°], 2.47 [25°], and 2.23 [50°] for $p\text{-CF}_3\text{C}_6\text{H}_4\text{CHClCH}_2\text{Cl}$, and 2.84 [0°], 2.60 [25°], and 2.42 for $p\text{-CF}_3\text{C}_6\text{H}_4\text{CTClCF}_3$. The KSIE in these cases result mainly from $\Delta\Delta H^\ddagger$ of 0.6 kcal/mol with the $\Delta\Delta S^\ddagger$ less than 0.7 eu, Table 2. Therefore the energetics associated with the desolvation of methoxide ion are part of the measured reaction energetics and should be the same for these reactions studied in methanol.

Activation Entropies. To compare rates of bimolecular reactions that differ by several orders of magnitude, we routinely measure kinetics over a $30\text{--}50$ °C range. To anticipate what to expect for two molecules reacting in the rate-limiting step,

(30) A referee pointed out that the element effect on k_1 suggests negative ion hyperconjugation in the transition structure since the electronegativity of Cl vs Br should give the reverse order. The same would hold true for the case of F vs Cl. A publication that appeared after this manuscript was submitted gives additional computational evidence for negative ion hyperconjugation by a β C-F [Sanuders, W. H., Jr. *J. Org. Chem.* **1997**, 62, 244].

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(32) (a) More O'Ferrall, R. A. *Chem. Commun.* **1969**, 114. (b) Gold, V.; Grist, S. *J. Chem. Soc. (B)* **1971**, 1665. (c) Gold, V.; Morris, K. P.; Wilcox, C. F. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1615.

Table 5. Rate Constants and Activation Parameters for Methanolic Sodium Methoxide-Promoted Dehydrochlorination Reactions

compd	k , $M^{-1} s^{-1}$ (0 °C)	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu (25 °C)	temp range, °C [no. of points]
<i>o</i> -CH ₃ C ₆ H ₄ CHClCF ₂ Cl	1.60×10^{-5}	21.81 ± 0.08	-0.5 ± 0.2	25 to 65 [8]
<i>o</i> -CF ₃ C ₆ H ₄ CHClCF ₂ Cl	4.21×10^{-5}	18.90 ± 0.03	-9.2 ± 0.1	20 to 60 [9]
2,6-Cl ₂ C ₆ H ₃ CHClCF ₂ Cl	8.78×10^{-5}	18.60 ± 0.03	-8.8 ± 0.1	10 to 60 [8]
2-Cl-6-FC ₆ H ₃ CHClCF ₂ Cl	1.74×10^{-4}	19.25 ± 0.05	-5.1 ± 0.2	10 to 45 [8]
<i>o</i> -ClC ₆ H ₄ CHClCF ₂ Cl	1.94×10^{-4}	19.44 ± 0.06	-4.2 ± 0.2	15 to 40 [6]
<i>p</i> -CH ₃ C ₆ H ₄ CHClCF ₂ Cl	2.28×10^{-4}	20.94 ± 0.03	1.6 ± 0.1	5 to 45 [12]
<i>m</i> -CH ₃ C ₆ H ₄ CHClCF ₂ Cl	4.01×10^{-4}	20.48 ± 0.07	1.1 ± 0.3	0 to 40 [8]
<i>o</i> -FC ₆ H ₄ CHClCF ₂ Cl	7.03×10^{-4}	19.43 ± 0.04	-1.6 ± 0.2	0 to 40 [6]
C ₆ H ₅ CHClCF ₂ Cl	7.15×10^{-4}	20.04 ± 0.07	0.6 ± 0.2	0 to 45 [10]
2,6-F ₂ C ₆ H ₃ CHClCF ₂ Cl	8.21×10^{-4}	18.27 ± 0.07	-5.6 ± 0.3	-5 to 30 [6]
<i>p</i> -FC ₆ H ₄ CHClCF ₂ Cl	1.16×10^{-3}	20.16 ± 0.07	2.0 ± 0.3	-10 to 30 [6]
2,4-Cl ₂ C ₆ H ₃ CHClCF ₂ Cl	1.64×10^{-3}	18.24 ± 0.08	-4.3 ± 0.3	-5 to 25 [7]
2,4-F ₂ C ₆ H ₃ CHClCF ₂ Cl	1.75×10^{-3}	19.03 ± 0.10	-1.3 ± 0.3	-10 to 20 [8]
<i>p</i> -ClC ₆ H ₄ CHClCF ₂ Cl	5.47×10^{-3}	19.00 ± 0.04	0.8 ± 0.1	-20 to 20 [15]
<i>m</i> -FC ₆ H ₄ CHClCF ₂ Cl	1.25×10^{-2}	18.71 ± 0.03	1.4 ± 0.1	-25 to 5 [7]
<i>m</i> -ClC ₆ H ₄ CHClCF ₂ Cl	1.60×10^{-2}	18.21 ± 0.02	0.1 ± 0.1	-25 to 10 [9]
3,4-F ₂ C ₆ H ₃ CHClCF ₂ Cl	1.79×10^{-2}	18.41 ± 0.09	1.0 ± 0.3	-30 to 5 [6]
<i>m</i> -CF ₃ C ₆ H ₄ CHClCF ₂ Cl	3.71×10^{-2}	18.37 ± 0.09	2.4 ± 0.3	-25 to 0 [6]
<i>p</i> -CF ₃ C ₆ H ₄ CHClCF ₂ Cl	9.14×10^{-2}	17.84 ± 0.06	2.2 ± 0.2	-30 to 0 [8]
<i>m</i> -NO ₂ C ₆ H ₄ CHClCF ₂ Cl	2.10×10^{-1}	16.67 ± 0.10	-0.4 ± 0.4	-45 to -20 [3]
<i>p</i> -CNC ₆ H ₄ CHClCF ₂ Cl	7.67×10^{-1}	15.77 ± 0.03	-1.2 ± 0.1	-61 to -20 [4]
3,5-(CF ₃) ₂ C ₆ H ₃ CHClCF ₂ Cl	2.88	15.77 ± 0.04	1.5 ± 0.2	-65 to -30 [6]

the ΔS^\ddagger values obtained from the reactions of methanolic sodium methoxide with ring-substituted β,β -difluorostyrenes, $YC_6H_4CH=CF_2 + CH_3O^- \rightarrow \{YC_6H_4CHCF_2OCH_3\}^-$, were used.³³ The average ΔS^\ddagger for ten ring substituents used to calculate $\rho = 3.56 \pm 0.03$ (25 °C) is -14.3 ± 0.8 eu, the average ΔS^\ddagger for seven compounds not used to calculate ρ is slightly lower, -15.7 ± 0.8 eu, and the average ΔS^\ddagger for ten compounds with ortho substituents is -17.3 ± 1.2 eu. Experimental ΔS^\ddagger values calculated from the Arrhenius plots routinely have a standard deviation of less than 0.3 eu. Although methoxide-promoted dehydrochlorinations of $YC_6H_4CHClCF_2Cl$ are bimolecular reactions, the average $\Delta S^\ddagger \approx 1$ eu for the non-ortho substituted compounds is much larger than that for the alkene reactions, Table 5.

It was suggested that ΔS^\ddagger values vary with the amount of internal return and more favorable activation entropies occur as the amount of internal return increases.³⁴ The k^H/k^D of 1.1 to 1.2 for alkoxide-catalyzed exchange and elimination reactions of $C_6H_5C^HClCF_3$ and $C_6H_5C^H(CF_3)_2$ suggest a very large amount of internal return associated with these reactions, and result in ΔS^\ddagger values greater than 10 eu.³⁵ On the other hand, ethoxide-promoted dehydrohalogenations of $C_6H_5CH_2CH_2X$ [$X = Br$ or Cl] have substantial k^H/k^D values, no internal return, and ΔS^\ddagger values of about -7 eu. The stereochemistry of the elimination can play a major role in determining ΔS^\ddagger . Cristol and co-workers measured values of ΔS^\ddagger for the elimination of four isomers of benzene hexachloride, $C_6H_6Cl_6$ -1.0, 3.6, 6.5, and 20.2 eu.³⁶ The 20.2 eu value is for the only isomer unable to undergo antielimination as all the chlorines are trans to each other.

We have been unable to model the temperature behavior for the isotope effects associated with eliminations from $C_6H_5C^LHClCF_2Cl$ or $C_6H_5C^LHBrCF_2Br$. The major conformer of $C_6H_5CHBrCF_2Br$ (>98%) has the bromine atoms anti to each other, and the $H-C-C-Cl$ is not antiperiplanar in either of the two

major conformers of $C_6H_5CHClCF_2Cl$.³⁷ Therefore the leaving halogen might not be anti to the encounter complex, $CH_3O^- \cdots H-C$, and would require a 60° rotation to obtain the proper alignment.³⁸ Rotational barriers in highly halogenated compounds are between 9 and 14 kcal/mol,³⁹ and this could lead to a third step.⁴⁰ Elimination from $C_6H_5CH_2CF_2Cl$, which has two benzylic hydrogens, results in a decrease of ca. 8 eu in ΔS^\ddagger compared to $C_6H_5CHClCF_2Cl$. This is attributed to dehydrochlorination occurring with substantially less or no internal return.

The presence of bulky ortho substituents could hinder internal return, and cause a decrease in the values of ΔS^\ddagger . Seven substituents were used to determine $\rho = 3.69 \pm 0.05$ at 0 °C,⁴¹ and the average ΔS^\ddagger equals 1.0 ± 1.0 eu for the 13 non-ortho-substituted $YC_6H_4CHClCF_2Cl$ or $Y_2C_6H_3CHClCF_2Cl$ in Table 5. This changes dramatically for the nine compounds with one or two ortho substituents as ΔS^\ddagger values range from -0.5 to -9.2 eu. Values for *o*-CF₃C₆H₄CHClCF₂Cl [-9.2 eu] and 2,6-Cl₂C₆H₃CHClCF₂Cl [-8.8 eu] are lowest, while 2,4-F₂C₆H₃CHClCF₂Cl [-1.3 eu] and *o*-CH₃C₆H₄CHClCF₂Cl [-0.5 eu] result in the highest values. There is internal consistency: two *o*-F compounds [-1.6 and -1.3 eu] and two *o*-Cl compounds [-4.3 and -4.2 eu]. Values are larger with two ortho substituents: 2,6-difluoro [-5.6 eu], 2-chloro-6-fluoro [-5.1 eu], and 2,6-dichloro [-8.8 eu]. The trifluoromethyl group [-9.2 eu] is the largest and the only problem seems to be the *o*-methyl [-0.5 eu].⁴² Further work is in progress dealing with the effects of ortho substituents.

(37) Drysdale, J. J.; Phillips, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 319.

(38) The methoxide-promoted dehydrohalogenation of $C_6H_5C^LHBrCF_2Cl$ gives only anti-eliminations of 3HCl and 4HBr [Koch, H. F. In *Comprehensive Carbanion Chemistry*, Part C; Buncl, E., Durst, T., Eds.; Elsevier: Amsterdam, 1987; pp 333 and 334.]

(39) (a) Thompson, D. S.; Newmark, R. A.; Sederholm, C. H. *J. Chem. Phys.* **1962**, *37*, 411. (b) Weigert, F. J.; Winstead, M. B.; Garrels, J. I.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7359.

(40) One of the referees commented that this would be at odds with the Curtin-Hammett principle. Although this is true, the energetics of the rotational barriers and the competition with internal return may well be an example of the breakdown of this principle, which does not have a large amount of experimental backing.

(41) Substituents used were as follows: *p*-CH₃, *m*-CH₃, H, *p*-Cl, *m*-F, *m*-Cl, and *m*-CF₃. The ρ value for the reaction of $YC_6H_4CH=CF_2$ increases to 3.92 ± 0.04 at 0 °C.

(42) We are at a loss to explain the ΔS^\ddagger of -0.5 for *o*-methyl. The compound has been synthesized three times by different students and always results in virtually the same value for ΔS^\ddagger .

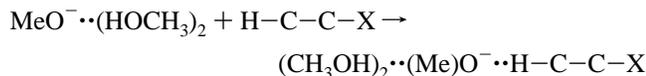
(33) The measurement of kinetic solvent isotope effect for these reactions has not been as extensive. However, the few that we have measured are about 2.0.

(34) See ref 17, pp 5425-27.

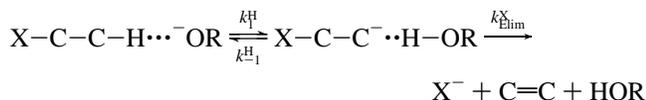
(35) Koch, H. F.; Dahlberg, D. B.; Lodder, G.; Root, K. S.; Touchette, N. A.; Solsky, R. L.; Zuck, R. M.; Wagner, L. J.; Koch, N. H.; Kuzemko, M. A. *J. Am. Chem. Soc.* **1983**, *105*, 2394.

(36) Cristol, S. J.; Hause, N. L.; Meek, J. S. *J. Am. Chem. Soc.* **1951**, *73*, 674.

Conclusions. Our working model for alkoxide-promoted dehydrohalogenation and hydron-exchange reactions is Scheme 1. For reactions with methanolic methoxide, the process starts after methoxide ion loses one molecule of solvation which allows it to form an encounter complex with the carbon acid.



The KSIE associated with the reaction, $k^{\text{OD}}/k^{\text{OH}} \approx 2.5$ at 25 °C, suggests the two remaining methanols are lost before reaching the transition structure leading to a hydrogen-bonded carbanion, k_1^{H} . This intermediate partitions between losing β -halide, $k_{\text{Elim}}^{\text{X}}$, or returning hydron to a negatively charged carbon, k_{-1}^{H} :



The hydrogen-bonded carbanion not only has the original C–H bond broken, but also has an elongated C–X bond. The latter conclusion comes from the analysis of chlorine isotope effects associated with elimination reactions of $\text{C}_6\text{H}_5\text{C}^i\text{HCICH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{C}^i\text{HCICF}_2\text{Cl}$.⁴³

Chloride and bromide can leave from the hydrogen-bonded intermediate as can fluoride when it leaves from a $-\text{CH}_2\text{F}$; however, when fluoride is part of a trifluoromethyl group, each C–F bond is stronger than that in a $-\text{CH}_2\text{F}$. This requires the formation of the free carbanion before F^- can depart to form an alkene. The near unity isotope effect for the exchange reactions of $p\text{-CF}_3\text{C}_6\text{H}_4\text{C}^i\text{HCF}_3$, $k^{\text{D}}/k^{\text{T}} = 1.08$ at 25 °C,⁴⁴ [similar values are reported for $\text{C}_6\text{H}_5\text{C}^i\text{H}(\text{CF}_3)_2$ and $\text{C}_6\text{H}_5\text{C}^i\text{HCCICF}_3$],³⁴ means that hydron transfer is not occurring in a rate-limiting step for the exchange reaction. Since the exchange is over 60 times faster than the elimination reaction, the barrier for the formation of a hydrogen-bonded intermediate is lower than that for loss of fluoride. The acidity of the benzylic C–H bonds should be about the same for $p\text{-CF}_3\text{C}_6\text{H}_4\text{CHCICF}_3$ and $p\text{-CF}_3\text{C}_6\text{H}_4\text{CHCICF}_2\text{Cl}$,⁴⁵ and result in similar rates of formation for the respective hydrogen-bonded intermediates. The element effect, $k^{\text{HCl}}/k^{\text{HF}}$ of 1.5×10^5 ,⁴⁶ has a $\Delta\Delta G^\ddagger$ of 7 kcal/mol, and this is not an unreasonable value for the breaking of a hydrogen bond.⁴⁷

For reactions of $m\text{-ClC}_6\text{H}_4\text{C}^i\text{HCICH}_2\text{X}$, a β -bromine accelerates the formation of the hydrogen-bonded carbanion by a factor of ≈ 19 over β -chlorine. The experimental element effect, $k^{\text{HBr}}/k^{\text{HCl}} = 29$, is largely due to the proton-transfer step, $k_1^{\text{HBr}}/k_1^{\text{HCl}} = 19$, rather than the formal breaking of the carbon–halogen

(43) Reference 1, p 1934, has a full discussion of this with additional references.

(44) The rate of exchange for $p\text{-CF}_3\text{C}_6\text{H}_4\text{CDCICF}_3$ with methanolic sodium methoxide at 25 °C is 8.58×10^{-4} with activation parameters of $\Delta H^\ddagger = 25.90 \pm 0.08$ and $\Delta S^\ddagger = 14.3 \pm 0.3$. Justin C. Biffinger, unpublished results.

(45) Relative rates of methoxide-promoted dehydrobromination of $\text{C}_6\text{H}_5\text{-CHBrCF}_2\text{Br}$, $\text{C}_6\text{H}_5\text{CHBrCFClBr}$, and $\text{C}_6\text{H}_5\text{CHCFBr}_2$ vary by a factor of 4, with the slowest being one diastereomer of $\text{C}_6\text{H}_5\text{CHBrCFClBr}$ and the fastest being the other diastereomer [Koch, H. F. In *Comprehensive Carbanion Chemistry: Ground and Excited State Reactivity*; Buncl, E., Durst, T., Eds.; Elsevier: Amsterdam, 1987; Part C, Chapter 6, p 330–335].

(46) The rate of dehydrofluorination of $p\text{-CF}_3\text{C}_6\text{H}_4\text{CHCICF}_3$ at 25 °C and activation parameters are given in Table 2. The activation parameters for $p\text{-CF}_3\text{C}_6\text{H}_4\text{CHCICF}_2\text{Cl}$ and rate at 0 °C are given in Table 5. The rate at 25 °C is $1.58 \text{ M}^{-1} \text{ s}^{-1}$.

(47) (a) Sano, T.; Tatsumoto, N.; Niwa, T.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2669. (b) Sano, T.; Tatsumoto, N.; Mende, Y.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2673.

bond. The competition between a loss of $\beta\text{-Cl}$ and internal return has an activation energy slightly favoring internal return and an A factor slightly favoring the loss of chloride, and this results in the moderate amounts of internal return, $k_{-1}^{\text{H}} \approx 0.6 k_{\text{Elim}}^{\text{Cl}}$. Dehydrobromination has a much more favorable activation energy for loss of $\beta\text{-Br}$ as well as the favorable A factor which results in a negligible amount of internal return, $k_{-1}^{\text{H}} \approx 0.05 k_{\text{Elim}}^{\text{Br}}$. Since the internal return does not affect the overall rate of dehydrobromination, the reactions of $m\text{-ClC}_6\text{H}_4\text{CHCICH}_2\text{-Br}$ and $m\text{-Cl}_6\text{H}_4\text{CHBrCH}_2\text{Br}$ could be classified as E2 mechanisms by at least one operational definition: *that the transition structure for the rate-limiting step has the β -hydrogen partially but not completely transferred and the C–X bond partially but not completely broken. This allows for the formation of some intermediates along the reaction pathway; however, the intermediates would not contribute to the kinetics or rate of the overall process.*⁴⁸

Since a $\beta\text{-Br}$ is more effective than a $\beta\text{-chloride}$ in accelerating the hydron-transfer step, it should carry more of the negative charge and has a weaker bond to carbon.⁴⁹ Removing the benzylic halide would place more charge on β -bromide and could result in even less internal return. The Arrhenius behavior of the isotope effect obtained for ethoxide-promoted dehydrobrominations of $\text{C}_6\text{H}_5\text{C}^i\text{H}(\text{CH}_3)\text{CH}_2\text{Br}$ was shown to be consistent with a reaction proceeding by Scheme 1. Swain–Schaad does not hold, $(k^{\text{H}}/k^{\text{T}}) \neq (k^{\text{D}}/k^{\text{T}})^{3.26}$, and the temperature dependence was modeled by using $A_{\text{Elim}}^{\text{Br}}/A_{-1} = 0.1$, $E_{-1}^{\text{D}} - E_{-1}^{\text{H}} = 1340$ cal/mol, and $E_{-1}^{\text{H}} - E_{\text{Elim}}^{\text{Br}} = 1950$ cal/mol.⁵⁰ The fit is good with $\mathbf{a}^{\text{H}} = 0.39$ at 25 °C; however, the $A_{\text{Elim}}^{\text{Br}}/A_{-1}$ favoring internal return is inconsistent with the A_{Elim}/A_{-1} used for the analyses in this study. The Arrhenius behavior, $A^{\text{H}}/A^{\text{D}} = 0.4$, has been attributed to quantum-mechanical tunneling occurring during an E2 mechanism.¹⁵ Some preliminary studies with $\text{C}_6\text{H}_5\text{C}^i\text{H}(\text{CH}_3)\text{CH}_2\text{Cl}$ did not give satisfactory kinetics over a reasonable temperature range to see if this system behaves similar to $\text{C}_6\text{H}_5\text{C}^i\text{H}_2\text{CH}_2\text{Cl}$. Work is in progress with $\text{YC}_6\text{H}_4\text{C}^i\text{H}(\text{CH}_3)\text{CH}_2\text{Cl}$ compounds with electron withdrawing groups to enhance reactivity and obtain better rate measurements.

Experimental Section

Materials. All starting materials were purchased from Aldrich. Solutions of alcoholic sodium alkoxide were made from the reaction of sodium with anhydrous alcohol. Deuterated alcohols were purchased from Aldrich and used without further purification. NMR spectra were recorded with several instruments. Early 60-MHz ¹⁹F spectra were obtained from a Varian HA-60 IL and ¹H spectra were obtained with a Varian T-60. Recent spectra have been obtained by using a Varian XL 300-MHz FT-NMR. A Varian VISTA system with 6 ft 0.25 or 0.06 in. packed columns with 15–20% SE-30 or OV 101 on 60/80 Chromasorb W was initially used to analyze kinetic samples. A HP 4600 with a 30 m RSL-150 polydimethylsiloxane (OV 101) with 0.53 mm i.d. and 1.2 μm film thickness is currently being used and gives much better results.

Synthesis of $\text{YC}_6\text{H}_4\text{C}^i\text{HCICH}_2\text{F}$. A three-step synthesis started with $\text{YC}_6\text{H}_4\text{MgBr}$ and $\text{FCH}_2\text{C}\equiv\text{N}$ to give a ketone, $\text{YC}_6\text{H}_4\text{COCH}_2\text{F}$, which was reduced by NaBH_4 after purification by column chromatography. The $\text{YC}_6\text{H}_4\text{C}^i\text{HOHCH}_2\text{F}$ was converted to $\text{YC}_6\text{H}_4\text{C}^i\text{HCICH}_2\text{F}$ by reaction with $(\text{C}_6\text{H}_5)_3\text{P}$ and CCl_4 . Yields for the first step ranged from 60% to 80%. Although yields for the last two steps were variable, they can each be carried out in >90% yield.

(48) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19.

(49) A referee states: "It is assumed that the faster reaction with $\beta\text{-Br}$ than $\beta\text{-Cl}$ is a result of more bond breaking to halogen at the transition state: it seems at least possible that much of this rate effect could come from relief of two serious gauche interactions as the α -carbon moves from sp^3 to sp^2 hybridization."

(50) Reference 11, p 6106.

1. ***p*-CF₃C₆H₄COCH₂F.** 4-Bromobenzotrifluoride (12.4 g, 55 mmol) in 100 mL of ether was added dropwise to 1.3 g (55 mmol) of Mg in 25 mL of ether. After the addition was completed, the reaction mixture was refluxed for 30 min and then allowed to cool to room temperature prior to the dropwise addition of 2.95 g (50 mmol) of fluoroacetonitrile in 50 mL of ether. The reaction mixture was cooled to 0 °C before adding 50–75 mL of 1 M HCl, which dissolves the precipitate formed during the reaction. After separation, the aqueous layer was extracted twice with 50 mL of ether. The combined ethereal layers were washed with water until neutral and 50 mL of saturated CaCl₂ and the dried over MgSO₄. Ether was removed by a rotary evaporator. The remaining organic material was purified by using a column of silica gel and 20% ether/hexane to yield 6.6 g (32 mmol, 64%) of a yellow oil that was used in the next step. The ¹H MNR at 60 MHz has a doublet due to the –CH₂F at 5.5 ppm with a *J*_{H–F} of 47 Hz, and the usual pattern for para substitution in the aromatic region.

2. ***p*-CF₃C₆H₄CHOHCH₂F.** 2-Fluoro-4'-trifluoroacetophenone (3.0 g, 14.6 mmol, 1.0 equiv) in 10 mL of ethanol was added dropwise to a solution of 0.3 g (7.3 mmol, 2.0 equiv) of NaBH₄ in 50 mL of ethanol and warmed to 50 °C for 30 min. Addition of 25 mL of 3 M HCl dissolved the precipitate formed during the reaction, and the resulting mixture was added to 200 mL of ice water and extracted four times with 50 mL of CH₂Cl₂. The combined methylene chloride layers were washed three times with ice water and dried over MgSO₄. Removal of the CH₂Cl₂ by a rotary evaporator left 3.7 g of residue that consisted of ≈3 g of product and ≈0.7 g of ethanol. This mixture was used in the last step, and the amount of (C₆H₅)₃P used was adjusted for any ethanol in the sample.

3. ***p*-CF₃C₆H₄CHClCH₂F.** The 3.7-g product from the previous reaction was refluxed with 6.5 g (24.8 mmol) of (C₆H₅)₃P and 50 mL of CCl₄ for 4 h. A precipitate formed and a GC of the CCl₄ layer showed no residual alcohol.⁵¹ The CCl₄ was removed by distillation, and the remaining mixture was codistilled with water. The two layers of the distillate were separated after adding 10 mL of CH₂Cl₂, and the aqueous layer was extracted twice with 10 mL of CH₂Cl₂. The combined CH₂Cl₂ layers were dried over MgSO₄ prior to removal of the CH₂Cl₂ by a rotary evaporator. The remaining 3.0 g of colorless liquid were used for kinetics. The ¹H MNR at 60 MHz has a doublet of doublets for the –CH₂F at 4.6 ppm with a *J*_{H1–H2} of 6 Hz and a *J*_{H2–F} of 47 Hz, and a multiplet for the benzylic proton at ≈5.0 ppm, which overlaps with the upfield part of the –CH₂F signal. The ¹⁹F NMR at 200 MHz has a doublet of triplets at 211.7 ppm with a *J*_{H2–F} of 47 Hz and *J*_{H1–F} of 13 Hz. The ¹H 60-MHz spectrum of *p*-CF₃C₆H₄CDClCH₂F is much cleaner with –CH₂F at 4.6–4.7 ppm and *d* with *J*_{H–F} = 47 Hz.

Synthesis of Styrenes. Substituted styrenes and β,β-difluorostyrenes are the precursors of the dichloro, dibromo, and bromochloro compounds used in this study. β,β-Difluorostyrenes were made by following a procedure similar to that reported for the synthesis of 2-(*p*-chlorophenyl)pentafluoropentene (method II).⁵² This is a Wittig type reaction of (C₆H₅)₃PCF₂CO₂Li [made *in situ* from ClCF₂CO₂Li and (C₆H₅)₃P] and the substituted benzaldehyde with dimethylformamide as solvent. The phosphonium salt is used in *n* excess [from 1.3 to 2.0] to ensure complete reaction of the aldehyde. After the reaction is complete, the alkene is codistilled with water from the dark reaction mixture. The lower layer is separated and dried over CaSO₄. The yields range from 40% to 60%, and the alkenes are pure enough for the next step without further purification.

The synthesis of YC₆H₄C'H=CH₂ [H = D or T] started with a reduction of YC₆H₄COCH₃ with NaB'H₄ to make YC₆H₄C'HOHCH₃, which was dehydrated using KHSO₄ to give the substituted styrene, YC₆H₄C'H=CH₂.⁵³ When ¹H = H, a Grignard reaction of YC₆H₄MgBr and CH₃CHO yielded YC₆H₄CHOHCH₃ directly. The dehydration occurred with variable yields, but was favored for deuterium or tritium incorporation over our old procedure *via* a dithiane to obtain the YC₆H₄C'HO followed by a Wittig reaction.¹ When possible, YC₆H₄–

CH=CH₂ was purchased. Deuterium and tritium incorporation for β,β-difluorostyrenes still made use of dithianes.

1. ***m*-ClC₆H₄CD(OH)CH₃.** *m*-Chloroacetophenone (24.8 g, 161 mmol, 1.0 equiv) was added dropwise to a solution of 1.97 g (47 mmol, 1.17 equiv) of NaBD₄ dissolved in 30 mL of 95% ethanol at a rate to keep the reaction below 50 °C. A white solid is formed during the addition. After 45 min of stirring, 60 mL of 3 M HCl was added to dissolve the precipitate. The solution was heated (to evaporate ethanol) until two distinct layers formed. After the layers separated, the aqueous layer was washed twice with 25 mL of CH₂Cl₂. The combined organic layers were washed four times with 25 mL of cold water to remove any remaining ethanol and dried over MgSO₄. The CH₂Cl₂ was removed by a rotary evaporator, and the resulting 18.6 g (118 mmol, 73% yield) of *m*-ClC₆H₄CD(OH)CH₃ was 99% pure according to gas chromatography. The proton MNR at 60 MHz had signals at 1.3 (3H, s), 4.2 (1H, s), 7.1 (3H), and 7.2 ppm (1H) for the aromatic protons.

2. ***m*-ClC₆H₄CD=CH₂.** *m*-ClC₆H₄CD(OH)CH₃ (4.48 g, 28 mmol, 1.0 equiv), 2.61 g of KHSO₄, 0.05 g of 4-*tert*-butylcatechol, and a magnetic stir bar were placed in a 50-mL single neck 24/40 round bottom flask fitted with a Claisen head that had a vacuum takeoff with a 50-mL round bottom flask receiver. Heat was applied by a 100 mL heating mantle filled with sand around the reaction flask. Maximum voltage was applied to rapidly raise the temperature of the sand to >200 °C over a period of 8–10 min. A vacuum of 160 to 180 mmHg was applied and the receiver was immersed in a Dewar with liquid nitrogen. Distillate came over between 60 and 75 °C. The 2.85 g (20 mmol) of *m*-ClC₆H₄CD=CH₂ was separated from the codistilled water, and the GC gave the purity of 98%. The proton MNR at 60 MHz had signals for the vinyl hydrogens at 5.1 (1H), 5.5 (1H), 7.1 (3H), and 7.2 ppm (1H) for the aromatics. A second run started with 7.04 g of *m*-ClC₆H₄CD(OH)CH₃ and 5.42 g of KHSO₄ and resulted in a yield of only 48%. It has been our experience that the best yields are obtained when under 5 g of starting alcohol is used.

Synthesis of YC₆H₄C'HCICH₂Cl. Initially the chlorination of styrenes was carried out in CCl₄; however, this method can form up to 30% YC₆H₄CHClCHCl₂ as an impurity.¹ An alternate method with dimethylformamide, DMF, as the solvent was used for most of the YC₆H₄C'HCICH₂Cl in this study.⁵⁴ This gave a significant reduction in the amount of the trichloride (2–5%). These small amounts of YC₆H₄CHClCHCl₂ did not interfere with the kinetics since YC₆H₄CCl=CHCl and YC₆H₄CH=CCl₂ formed by dehydrohalogenation had different retention times in the gas chromatographic analysis of kinetic samples. Since it is 30 times more reactive, the trichloride does not interfere with the dichloride tritium kinetics and only results in a slightly higher infinity point activity due to the small amount of YC₆H₄CT=CCl₂ formed.

***m*-ClC₆H₄CDClCH₂Cl.** *m*-ClC₆H₄CD=CH₂ (2.8 g, 20 mmol) was dissolved in 15 mL of DMF in a 50 mL round-bottom flask with a stir bar and placed in an ice bath. Chlorine (1.4 g, 20 mmol) was condensed into the reaction flask. The reaction mixture was stirred for 30 min at room temperature before a short path distillation head replaced the reflux condenser prior to vacuum distillation. *m*-ClC₆H₄CDClCH₂Cl (2.9 g, 14 mmol, 69% yield) was collected between 108 and 120 °C at 7 mmHg. The 300 MHz ¹H MNR has an AB pattern for the –CH₂Cl at 3.9 ppm with *J*_{A–B} = 11 Hz. The –CH₂Cl of *m*-ClC₆H₄CHClCH₂Cl has an ABX pattern at 3.9 to 4 ppm with *J*_{A–X} = 6 Hz, *J*_{B–X} = 8 Hz, and *J*_{A–B} = 11 Hz, and the benzylic proton has a *d* of *d* at 5.0 ppm. *m*-ClC₆H₄CDClCHCl₂ has a singlet at 5.95 ppm, and *m*-ClC₆H₄CHClCHCl₂ has two doublets at 5.2 and 6.0 ppm with a *J* ≈ 8 Hz.

Synthesis of *m*-ClC₆H₄CHBrCH₂Br. *m*-ClC₆H₄CH=CH₂ (3.5 g, 27 mmol) and 35 mL of CCl₄ were placed in a 125 mL Erlenmeyer flask with a magnetic stir bar. A solution of 4.3 g (27 mmol) of Br₂ and 2 mL of CCl₄ was added dropwise, and the resulting mixture was stirred overnight. After the CCl₄ was removed the product was purified by column chromatography by using a silica gel column and a 1:1 ratio of hexanes:CH₂Cl₂. The 4.0 g (49% yield) of *m*-ClC₆H₄CHBrCH₂Br had a mp of 42.5 to 44 °C. The 300 MHz NMR has an ABX pattern for the non-aromatic protons: H_X at 5.1 ppm (*J*_{A–X} = 5 Hz, *J*_{B–X} = 11 Hz); H_A at 4.0 ppm (*J*_{A–B} = 11 Hz); H_B at 3.9 ppm. The *m*-ClC₆H₄–

(51) The extent of reaction has also been followed by the disappearance of the OH proton using proton NMR.

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CDBrCH₂Br resulted in the absence of the signal at 5.1 ppm, with an AB pattern at 4.0 ppm (2H, $J_{A-B} = 11$ Hz).

Synthesis of *m*-ClC₆H₄CDClCH₂Br. A 250 mL Erlenmeyer flask was charged with 26 mL of water, 26 mL of 12 M HCl, and a magnetic stir bar and placed in an ice/water bath. While the solution was stirred small portions of 17.5 g (126 mmol) of *m*-chlorostyrene and 17.3 g (126 mmol) of *N*-bromosuccinamide were added alternately and formed a second layer.⁵⁵ The aqueous layer was washed three times with 25 mL of CH₂Cl₂ and combined with the original organic layer. This was washed once with 25 mL of 5% NaHCO₃, twice with 25 mL of 20% Na₂S₂O₅, and three times with water and dried over MgSO₄. The CH₂-Cl₂ was removed by a rotary evaporator prior to vacuum distillation. After preliminary distillation, the combined cuts were carefully redistilled and a center cut, 138–140 °C at 12–13 mmHg, was still found to contain about 17% of the dibromide, *m*-ClC₆H₄CDBrCH₂Br. The 60 MHz ¹H NMR had the -CH₂Br at 3.9 for *m*-ClC₆H₄CDClCH₂-Br and at 4.0 for *m*-ClC₆H₄CDBrCH₂Br.

Since neither the *m*-ClC₆H₄CDBrCH₂Br nor the reaction products, *m*-ClC₆H₄CB=CH₂ or *m*-ClC₆H₄CD=CHBr, interfere with the GC analysis, this sample was used for kinetic runs. The product ratios for the synthesis of *m*-ClC₆H₄CHClCH₂Br was similar to that for the deuterium compound.

Synthesis of YC₆H₄CHClCF₂Cl. The chlorination reaction of C₆H₅-CH=CF₂ dissolved in CCl₄ has been described in detail.⁵⁶ The ¹⁹F 60 MHz NMR spectra of all the YC₆H₄CHClCF₂Cl shows a clear ABX pattern: F_A at 57–58 ppm, F_B at 61–62 ppm, $J_{A-H} \approx 7$ Hz, $J_{B-H} \approx 10$ Hz, and $J_{A-B} = 162-164$.

Kinetics of Hydrogen and Deuterium Compounds. Dehydrohalogenation kinetics were carried out under pseudo-first-order conditions with ratios of alkoxide to substrate larger than 15 to 1. A solution of alcoholic sodium alkoxide solution [30–40 mL \approx 0.3 M] in a 50-mL Erlenmeyer capped with a serum stopper was allowed to reach temperature in a bath held to ± 0.1 °C. The reactant, 25–75 μ L, and a standard, 15–50 μ L, were mixed and injected into the solution by a 1-mL glass Luer-lok syringe equipped with a 4 in. stainless steel needle. Disposable glass or plastic 5-mL syringes fitted with 4-in. stainless steel needles were used to take 3–4-mL samples that were injected

into about 100 mL of dilute aqueous HCl and extracted with 0.25 to 1 mL of CCl₄ with use of a 125 mL separatory funnel with a Teflon stopcock. After vigorous shaking for about a minute, the layers were allowed to separate [usually waiting 15–20 min] and the CCl₄ layer was analyzed with an automated gas chromatographic instrument. A typical run consisted of nine samples and an infinity point. The advantage of using gas chromatography to analyze the samples is that both the disappearance of substrate and the appearance of products can be followed.

Kinetics of Tritium Compounds. The detritiohalogenation and exchange reactions were run with <10 μ L substrate in 12–15 mL methanolic sodium methoxide. Aliquots were taken with a 1 mL glass or plastic syringe fitted with a 4-in. stainless steel needle. Nine points and an infinity sample were taken. Samples for a given run were of the same size [0.85 to 0.95 mL] and were injected into 75 mL of dilute aqueous HCl and extracted with 10.0 mL of toluene by using a 125 mL separatory funnel with a Teflon stopcock. The mixture was shaken for the same length of time [30–60 s] and allowed to stand for 20 min before the layers were separated. The toluene layer was dried for 20 min with Drierite. A 5.0-mL sample of the dried toluene was mixed with 5 mL of a scintillation cocktail [INSTA-FLUOR (TM) or OPTI-FLUOR (R)] and counted with a Packard Tri-Carb 4640.

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