Comparison of gas-phase acidities of some carbon acids with their rates of hydron exchange in methanolic methoxide

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ABSTRACT: Hydron exchange reaction rates, $k_{exch}\,M^{-1}s^{-1}$, using methanolic sodium methoxide are compared with gas-phase acidities, ΔG^0_{Acid} kcal/mol, for four 9-YPhenylfluorenes-9-^{i}H, seven $YC_6H_4C^iH(CF_3)_2$, seven $YC_6H_4C^iHClCF_3$, and $C_6F_5{}^iH$. Fourteen of the fluorinated benzylic compounds and pentafluorobenzene result in near unity experimental hydrogen isotope effects that suggest substantial amounts of internal return associated with the exchange process. Although the reactions of 9-phenylfluorene have experimental isotope effects that appear to be normal in value, they do not obey the Swain–Schaad relationship. This suggests that they occur with small amounts of internal return. The entropies of activation, $\Delta S^{\ddagger}$, are +12 to +14 eu, for the benzylic compounds and different significantly from those for the 9-YPhenylfluorenes, $\Delta S^{\ddagger}$ of −8 to −12 eu. The $\Delta S^{\ddagger} \sim 1$ eu for the reactions of pentafluorobenzene falls between the other compounds. Density functional calculations using B3LYP/6-31+G(d,p) are reported for the reactions of $CH_3O^-(HOCH_3)_3$ with C_6F_5H, $C_6H_5CH(CF_3)_2$, $C_6H_5CHClCF_3$, and 9-phenylfluorene. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: kinetic acidities; methanolic sodium methoxide; ΔG^0_{Acid} (gas phase); B3LYP/6-31+G(d,p) calculations

INTRODUCTION

Over 30 years ago Ritchie[1] predicted that carbon acids whose conjugate bases have localized charge will have their rates of hydron exchange ['kinetic acidities'] greater than their thermodynamic acidities. An example is the weaker acid pentafluorobenzene-*t* [**PFB**-*t*], $pK_a = 25.8$,[2] has a methoxide catalyzed protodetritiation rate, $k = 2.57 \times 10^{-2}\,M^{-1}s^{-1}$,[3] that is 15 times faster at 25 °C than that for 9-phenylfluorene-9-*t* [**9-PhFl-9-*t***], $pK_a = 18.5$ and $k = 1.77 \times 10^{-3}\,M^{-1}s^{-1}$.[4] Reactions of **PFB-^{i}H** result in forming $C_6F_5{}^-$ [**PFB$^-$**] with lone pair electrons in an sp^2 orbital, while the aromatic 9-phenylfluorenyl anion [**9-PhFl$^-$**] is highly π-delocalized. The unity primary kinetic isotope effect [PKIE], $k^D/k^T = 1.0$, for the exchange reactions of **PFB^{i}H** differs from the k^D/k^T of 2.54 obtained from the reactions of

9-PhFl-9-^{i}H. Cram first suggested that near unity isotope effects for hydron exchange reactions are due to an internal-return mechanism with hydron transfer occurring prior to the rate-limiting step in the reaction mechanism.[5] Therefore, after a correction for internal return, tritium transfer from the weaker acid, **PFB-*t***, to $^-OCH_3$ is at least 750 times faster than that from the stronger acid, **9-PhFl-9-*t***.

Our correlation of gas-phase acidities, ΔG^0_{Acid}, and rates of methanolic sodium methoxide catalyzed hydron exchange reactions has been extended from the first report[6] and now includes a number of phenyl-ring-substituted 9-phenylfluorenes, $C_6H_5C^iH(CF_3)_2$ [**I**] and $C_6H_5{}^iHClCF_3$ [**II**], Table 1. Density functional calculations using B3LYP/6-31+G(d,p) are also reported to compare the energies and charge distribution of possible intermediates formed during the reactions of methanolic methoxide with **9-PhFl**, **PFB**, **I** and **II**.

RESULTS AND DISCUSSION

A general scheme for the methoxide-catalyzed exchange of R-D starts when it is aligned with the methoxide ion, EC-*d*. Two solvent methanols are included since calculations on hydron transfer between R-H and

Table 1. Experimental gas-phase acidities, ΔG^0_{Acid}, Rate constants and activation parameters for methanolic sodium methoxide promoted hydron exchange reactions

Compound	ΔG^0_{Acid}, kcal/mol	k, $M^{-1}s^{-1}$ (25°C)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu (25°C)	Temperature range °C [number of points]
m-CF$_3$C$_6$H$_4$CT(CF$_3$)$_2$	326.8	4.74 E-1	21.60 ± 0.10	12.4 ± 0.4	−19 to 0 [4]
m-CF$_3$C$_6$H$_4$CT(CF$_3$)$_2$ [MeOD]		1.33	20.63 ± 0.02	11.2 ± 0.1	−29 to −10 [3]
m-FC$_6$H$_4$CD(CF$_3$)$_2$	331.5	8.50 E-2	21.55 ± 0.08	8.8 ± 0.3	−10 to 15 [4]
p-ClC$_6$H$_4$CD(CF$_3$)$_2$	331.4	3.45 E-2	23.10 ± 0.16	12.2 ± 0.6	0 to 20 [5]
p-FC$_6$H$_4$CD(CF$_3$)$_2$	334.3	3.33 E-3	24.64 ± 0.16	12.8 ± 0.5	10 to 30 [5]
C$_6$H$_5$CD(CF$_3$)$_2$	335.3	2.12 E-3[a]	24.4 ± 0.1	11.2 ± 0.4	0 to 50 [7]
C$_6$H$_5$CT(CF$_3$)$_2$		2.09 E-3[a]	24.1 ± 0.2	9.9 ± 0.7	5 to 50 [7]
C$_6$H$_5$CT(CF$_3$)$_2$ [MeOD]		5.49 E-3[a]	23.9 ± 0.1	11.1 ± 0.2	5 to 50 [9]
C$_6$H$_5$CH(CF$_3$)$_2$ [MeOD]		6.14 E-3[a]	23.9 ± 0.1	11.4 ± 0.3	10 to 50 [5]
m-CH$_3$C$_6$H$_4$CD(CF$_3$)$_2$	336.3	1.04 E-3	24.97 ± 0.15	11.5 ± 0.5	20 to 40 [5]
p-CH$_3$C$_6$H$_4$CD(CF$_3$)$_2$	337.0	4.70 E-4	25.53 ± 0.20	11.9 ± 0.7	25 to 45 [5]
p-NO$_2$C$_6$H$_4$CDClCF$_3$	329.8	4.40	16.62 ± 0.05	0.1 ± 0.2	−50 to −30 [4]
p-NO$_2$C$_6$H$_4$CDClCF$_3$ [MeOD]		4.04 E+1	16.23 ± 0.19	3.2 ± 0.8	−55 to −40 [3]
3,5-(CF$_3$)$_2$C$_6$H$_3$CDClCF$_3$	332.4	7.51 E-2	22.48 ± 0.07	11.7 ± 0.3	−5 to 25 [6]
3,5-F$_2$C$_6$H$_3$CDClCF$_3$	340.5	1.82 E-3	25.36 ± 0.10	14.0 ± 0.4	10 to 30 [3]
p-CF$_3$C$_6$H$_4$CDClCF$_3$	337.4	8.58 E-4	25.90 ± 0.08	14.3 ± 0.3	20 to 45 [6]
p-CF$_3$C$_6$H$_4$CTClCF$_3$		7.91 E-4[b]	25.42 ± 0.08	12.5 ± 0.3	20 to 55 [8]
p-CF$_3$C$_6$H$_4$CTClCF$_3$ [MeOD]		2.06 E-3[b]	24.86 ± 0.13	12.5 ± 0.4	20 to 45 [6]
m-CF$_3$C$_6$H$_4$CDClCF$_3$	340.1	1.09 E-4	26.36 ± 0.11	11.7 ± 0.3	30 to 55 [7]
m-CF$_3$C$_6$H$_4$CTClCF$_3$		1.03 E-4	26.67 ± 0.12	12.7 ± 0.4	30 to 60 [5]
m-CF$_3$C$_6$H$_4$CTClCF$_3$ [MeOD]		2.77 E-4	25.81 ± 0.33	11.8 ± 1.1	30 to 50 [3]
m-CF$_3$C$_6$H$_4$CTClCF$_3$ [EtOH]		2.20 E-3	25.25 ± 0.16	14.0 ± 0.5	10 to 40 [7]
m-CF$_3$C$_6$H$_4$CHClCF$_3$ [MeOD]		3.03 E-4	25.51 ± 0.14	10.9 ± 0.5	30 to 50 [3]
m-ClC$_6$H$_4$CTClCF$_3$	343.2	4.16 E-5	26.96 ± 0.08	11.8 ± 0.3	35 to 59 [5]
m-ClC$_6$H$_4$CTClCF$_3$ [EtOH]		7.74 E-4	25.31 ± 0.16	12.1 ± 0.5	25 to 50 [5]
m-FC$_6$H$_4$CDClCF$_3$	344.6	2.36 E-5	27.85 ± 0.06	13.7 ± 0.2	40 to 65 [5]
C$_6$H$_5$CTClCF$_3$ [EtOH]	348.7	9.03 E-6[a]	26.54 ± 0.01	7.4 ± 0.1	50 to 80 [3]
9-(p-CF$_3$C$_6$H$_4$)-fluorene-9-t	326.9	2.03 E-2	15.78 ± 0.11	$-13.4 \pm .4$	−10 to 25 [4]
9-(m-CF$_3$C$_6$H$_4$)-fluorene-9-t [MeOD]	327.4	1.58 E-2	17.07 ± 0.06	$-9.5 \pm .2$	0 to 20 [3]
		3.38 E-2	16.29 ± 0.14	$-10.6 \pm .5$	−10 to 10 [3]
9-(m-FC$_6$H$_4$)-fluorene-9-t	331.3	8.24 E-3	17.84 ± 0.05	$-8.2 \pm .2$	0 to 25 [4]
9-Phenylfluorene-9-d	335.6[c]	3.89 E-3	17.22 ± 0.04	$-11.8 \pm .1$	5 to 35 [3]
9-Phenylfluorene-9-t		1.54 E-3	18.42 ± 0.13	$-9.6 \pm .4$	25 to 45 [5]
9-Phenylfluorene-9-t [MeOD]		3.25 E-3	18.13 ± 0.07	$-9.1 \pm .2$	25 to 40 [3]
9-Phenylfluorene-9-h [MeOD]		5.16 E-2	15.18 ± 0.07	$-13.5 \pm .3$	−25 to 5 [6]
CDCl$_2$CF$_3$	348.2	1.90 E-2[d]	21.3 ± 0.1	$5.0 \pm .3$	0 to 20 [2]
C$_6$F$_5$D	349.2	3.07 E-2	19.52 ± 0.19	$0.0 \pm .7$	0 to 21 [5]
C$_6$F$_5$T		2.96 E-2[e]	19.76 ± 0.07	$0.7 \pm .2$	−15 to 15 [6]
C$_6$F5T [MeOD]		5.93 E-2	19.45 ± 0.05	$1.1 \pm .2$	−20 to 15 [4]
C6F$_5$H [MeOD]		6.53 E-2	19.25 ± 0.07	$0.6 \pm .3$	−15 to 10 [4]

[a] Ref. 18. Rate constant is divided by 20 to corrected for reaction in methanolic sodium methoxide, $k \approx 4.5 \times 10^{-7}\,M^{-1}s^{-1}$.
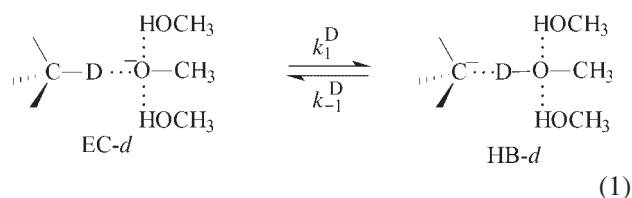
[b] Ref. 14.

[c] Bartmess, J. E.; *Negative Ion Energetics Data in NIST Standard References Database Number 69*, Lindstrom, P. J. and Mallard, W. G., Eds., NIST, Gathersburg, MD **2003**.

[d] Data from Ref. 26a used to calculate values at 25°C and activation parameters.

[e] Data from Ref. 3 give the following: C$_6$F$_5$T, $k = 2.57$ E-2 (25°C), $\Delta H^{\ddagger} = 19.92 \pm 0.05$ kcal/mol, $\Delta S^{\ddagger} = 1.0 \pm 0.2$ eu.

$^{-}$OCH$_3$ did not mimic solution experimental results. The deuterium can now be transferred to methoxide, k_1^D, to form the hydrogen-bonded carbanion, HB-d.

forward step that breaks the hydrogen bond to form FC-d, k_2^D, which is not stabilized by direct contact with the DOCH$_3$.

(1)

(2)

The internal-return step, k_{-1}^D, regenerates the deuterated carbon acid and methoxide and competes with a
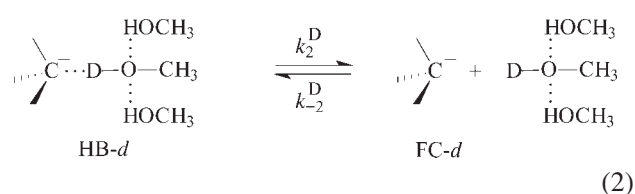
A rearrangement of the solvent molecules replaces the CH$_3$OD with a CH$_3$OH in the best position to form a new

hydrogen-bonded carbanion HB-*h*, k_3^H. The CH$_3$OD is lost in a sea of CH$_3$OH and formation of HB-*d*, k_{-2}^D, does not compete favorably with the formation of HB-*h* starting the process to give R-H.

(3)
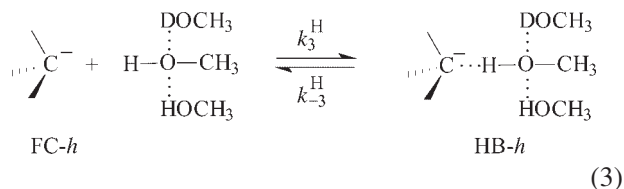
The rate law for this mechanism is:

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2}$$ (4)

There are two extremes for this rate law: (a) when $k_{-1} \gg k_2$, then $k_{obs} = [k_1/k_{-1}]k_2$, and (b) when $k_2 \gg k_{-1}$, then $k_{obs} = k_1$. For case (a) second-order kinetics and near unity experimental isotope effects are expected. For case (b) second-order kinetics are expected with normal experimental isotope effects that obey the Swain–Schaad relationship, $k^H/k^T = (k^H/k^D)^{1.442}$.[7]

A contribution to the analysis of isotope effects associated with cases where there is no single rate-limiting step was made by the Streitwieser group in 1971.[4,8] Using the rate constants for all three hydrogen isotopes at one temperature and the Swain–Schaad relationship, they can calculate an internal-return parameter, *a* = k_{-1}/k_2, for each isotope, and the rate constant for the hydron transfer steps can be calculated using:

$$k_1 = k_{obs}[a + 1]$$ (5)

This analysis was applied to the methoxide-catalyzed rates of the exchange reactions for **9-PhFl-9-*i*H** that resulted in $k^D/k^T = 2.53$ and $k^H/k^T = 15.9$.[9] To satisfy the Swain–Schaad relationship, the value of k^H/k^T should be 20.6 or 22.3.[10] The deviations from Swain–Schaad predict that a small amount of internal return is associated with the hydron exchange reactions of **9-PhFl-9-*i*H**. The internal return is negligible for **9-PhFl-9-*t*** ($a^T = 0.016$) and **9-PhFl-9-*d*** ($a^D = 0.050$), but cannot be ignored for **9-PhFl-9-*h*** ($a^H = 0.49$).[11]

Albery and Knowles[12] warned that very accurate isotope effects are required to make use of deviations from a rather insensitive Swain–Schaad relationship to calculate amounts of internal return. Dahlberg calculated the anticipated effect of an internal return mechanism on the Arrhenius behavior of the PKIE associated with hydron transfer reactions.[13] Since this analysis does not make use of the Swain–Schaad relationship, a temperature-dependence study on all three hydrogen isotopes offers an alternate method to determine the internal return process, and also gives information about the relative entropy and enthalpy relationship between the return step

and any forward step. We have used this in studies of alkoxide-promoted dehydrohalogenation reactions.[14]

Kinetic acidity versus thermodynamic acidity

The pK_a of carbon acids with beta C—F bonds cannot be measured in solution due to the rapid elimination of the beta fluoride ion. The elimination of a beta fluoride from **PFB$^-$** was slow enough to allow the measurement of a solution pK_a for **PFB**.[2] Carbon acids with a —CF$_3$ group attached to the acidic carbon atom form stable anions in the gas phase and permits measurement of gas-phase acidities, ΔG_{Acid}^0. Values for 15 ring substituted compounds of C$_6$H$_5$CH(CF$_3$)$_2$ [**I**] or C$_6$H$_5$CHClCF$_3$ [**II**] are given in Table 1. The gas-phase acidities for **I**, $\Delta G_{Acid}^0 = 335.3$ kcal/mol, and **9-PhFl**, $\Delta G_{Acid}^0 = 335.6$ kcal/mol, are about the same. Since the protodetritiation rates [kinetic acidity] for C$_6$H$_5$CT(CF$_3$)$_2$, $k = 2.09 \times 10^{-3}$ M^{-1}s^{-1}, and **9-PhFl-9-*t***, $k = 1.54 \times 10^{-3}$ M^{-1}s^{-1}, are virtually the same at 25°C, both kinetic and thermodynamic acidity are similar for the two compounds. This does not hold with substituents on the phenyl rings of **I** and **9-PhFl**, Fig. 1. The ΔG_{Acid}^0 values for ***m*-F-I**, 331.5 kcal/mol, and **9-*m*-FPhFl**, 331.3 kcal/mol, are still similar; however, the exchange rates for ***m*-F-I-*d***, $k = 8.50 \times 10^{-2}$ M^{-1}s^{-1}, and **9-*m*-FPhFl-9-*t***, $k = 8.24 \times 10^{-3}$ M^{-1}s^{-1}, differ by a factor of 10.[15] A Hammett plot using sigma values for the four **9-YPhFl-9-*t*** compounds in Table 1 results in a rho of 2.1, and suggests that the negative charge of the fluorenyl anions is not π-delocalized into the phenyl rings that are twisted and therefore cannot conjugate fully with any negative
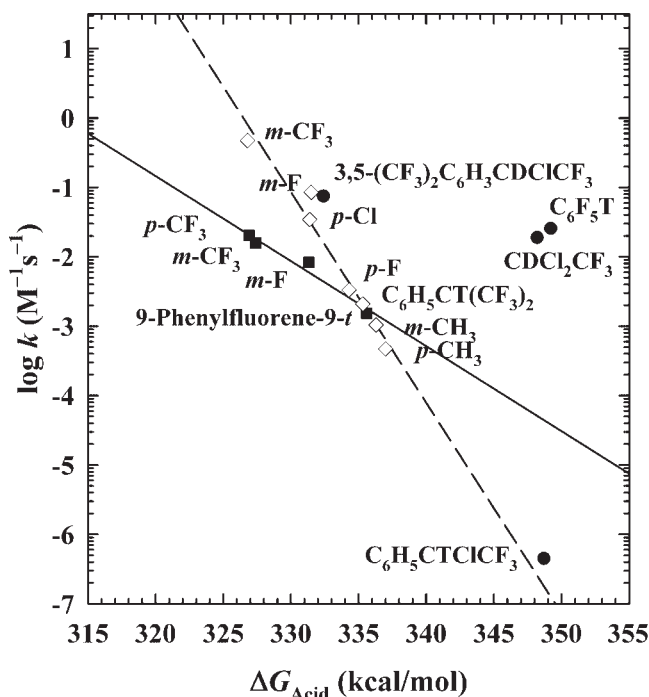
Figure 1. Correlation of experimental gas phase acidities and kinetic acidities

charge developing at the 9-carbon. Fujio and Tsuno reported small rho values for systems where the phenyl is twisted to hinder conjugation.[16] On the other hand, rates for the seven **Y-I** compounds result in a rho value of 4.9, and this is similar to one for the protodetritiation of ring-substituted toluene-α-t's with lithium cyclohexylamide in cyclohexylamine.[17]

The gas-phase acidities of **II**, $\Delta G^0_{Acid} = 348.7$ kcal/mol, and **PFB**, $\Delta G^0_{Acid} = 349.2$ kcal/mol, are similar. The protodetritiation of $C_6H_5CTClCF_3$ [**II-t**] is too slow in methanolic sodium methoxide and was carried out in ethanolic sodium ethoxide, $k = 9.03 \times 10^{-6} M^{-1}s^{-1}$. Reactions in methanolic sodium methoxide are about 20 times slower than those in ethanol [see m-$ClC_6H_4CTClCF_3$ and m-$CF_3C_6H_4CTClCF_3$ in Table 1]. When the ethoxide rate for the protodetritiation of **II-t** is corrected for the change in base systems, $k \approx 4.5 \times 10^{-7} M^{-1}s^{-1}$, the rate is about 66,000 times slower than that for **PFB-t**, $k = 2.96 \times 10^{-2} M^{-1}s^{-1}$, Fig. 1. To get a derivative of **II** close to the kinetic acidity of **PFB** requires the much stronger acid 3,5-$(CF_3)_2C_6H_3CDClCF_3$, $\Delta G^0_{Acid} = 332.4$ kcal/mol, which has a rate of deuterium exchange, $k = 7.51 \times 10^{-2} M^{-1}s^{-1}$, that is only 2.4 times faster than that for **PFB-d**.

There is no relationship between the kinetic and thermodynamic acidities when comparing the behavior of **Y-PhFl** or **PFB** with **Y-I** and **Y-II**. There are also large differences in the activation entropies, $\Delta S^{\ddagger}$, associated with their exchange kinetics. The four **Y-PhFl** compounds result in $\Delta S^{\ddagger}$ values between -8 and -14 eu, while the seven **Y-I** compounds and seven of the **Y-II** derivatives are at the other extreme with $\Delta S^{\ddagger}$ values between $+9$ and $+14$ eu. The reactions of **PFB** are in the middle with $\Delta S^{\ddagger} \approx +1$ eu. With the exception of **p-NO$_2$-II**, the **Y-I** and **Y-II** compounds have near unity experimental PKIE values similar to that for **PFB**, while the **9-PhFl** has 'normal' PKIE values that suggest a small amount of internal return.

Activation entropies and experimental PKIE values associated with the exchange reactions

Our initial studies of the reactions of **I** used both ethanolic sodium ethoxide and methanolic sodium methoxide for hydron exchange and dehydrofluorination reactions. Twelve different temperature dependence studies using ≈ 0.3 M alkoxide solutions resulted in near unity PKIE values and $\Delta S^{\ddagger}$ values of $+10$ to $+18$ eu.[18] Therefore, a working model is that hydron-transfer reactions associated with near unity PKIE have $\Delta S^{\ddagger}$ values near or above $+10$ eu. This holds for the reactions of the $YC_6H_4 C^iH(CF_3)_2$ compounds and seven of the $YC_6H_4C^iHClCF_3$ derivatives. The exception is the reactions of **p-NO$_2$-II** with $\Delta S^{\ddagger}$ values between 0 and $+2$ eu, and a $k^H/k^D \approx 3$

after correcting for a solvent isotope effect of $k^{OD}/k^{OH} = 2.6$. This is probably due to the formation of a more π-delocalized carbanion that has less internal return than the reactions of the other **Y-II** compounds. The $\Delta S^{\ddagger}$ value increases to $+15$ eu for the dehydrofluorination of p-$NO_2C_6H_4CHClCF_3$ which is 1300 times slower, $k = 3.33 \times 10^{-3} M^{-1}s^{-1}$ at 25°C, than the exchange reaction of p-$NO_2C_6H_4CDClCF_3$, $k = 4.40 M^{-1}s^{-1}$ at 25°C. In contrast to this the methoxide-catalyzed exchange reaction of p-$CF_3C_6H_4CDClCF3$ is only 75 times faster than the dehydrofluorination of p-$CF_3C_6H_4CHClCF_3$ which has a similar value of $\Delta S^{\ddagger} = +12.3$ eu. A larger difference in $\Delta S^{\ddagger}$ between a dehydrofluorination reaction, $\Delta S^{\ddagger} = +10$ eu, and exchange reaction, $\Delta S^{\ddagger} = -17$ eu, was reported for 9-trifluoro-methylfluorene, and these reactions form a highly π-delocalized carbanion.[19]

The $\Delta S^{\ddagger}$ values for the **9-YPhFl-9-t** compounds are between -8 and -14 eu, and the experimental isotope effects associated with the reactions of **9-PhFl** suggest only a small amount of internal return. These $\Delta S^{\ddagger}$ values are more consistent with the second order-kinetics expected from bimolecular reactions featuring a small amount of internal return. Our model for $\Delta S^{\ddagger}$ values expected for bimolecular reactions occurring with methanolic sodium methoxide comes from the reactions of CH_3O^- and 13 $CF_2{=}CHC_6H_4Y$ compounds that form intermediates, $\{CH_3OCF_2CHC_6H_4Y\}^-$, in the rate-limiting step and have no return to starting materials. The experimental $\Delta S^{\ddagger}$ values associated with these reactions range from -15 to -20 eu.[20]

The methoxide-promoted dehydrofluorinations of p-$CF_3C_6H_4C^iHClCH_2F$ [$^iH = H$, D, and T] result in $\Delta S^{\ddagger} = +2.6$ eu, with $k^H/k^D = 2.19$ and $k^D/k^T = 1.63$ at 25°C, internal-return parameters of $a^H = 2.1$, $a^D = 0.50$ and $a^T = 0.27$, and have no exchange with solvent prior to elimination. The loss of fluoride from a —CH_2F can occur from a hydrogen-bonded carbanion while loss of fluoride from a —CF_3 requires the formation of a free carbanion which accepts a hydron from solvent faster than ejecting the fluoride ion.[14] The methoxide-promoted eliminations of HCl from m-$CF_3C_6H_4C^iHClCH_2Cl$ have $\Delta S^{\ddagger} = -1.7$ eu, with $k^H/k^D = 3.49$ and $k^D/k^T = 1.88$ at 25°C resulting in values of $a^H = 0.59$, $a^D = 0.13$, and $a^T = 0.068$. Similar reactions for m-$ClC_6H_4C^iHClCH_2Cl$ have $\Delta S^{\ddagger} = -2.6$ eu with $k^H/k^D = 3.49$ and $k^D/k^T = 1.83$ at 25°C resulting in values of $a^H = 0.59$, $a^D = 0.14$, and $a^T = 0.072$.[14] The dehydrochlorination reactions of 13 $YC_6H_4CHClCF_2Cl$ compounds with one or two *meta* or *para* substituents result in an average $\Delta S^{\ddagger}$ of about 1 eu. The $\Delta S^{\ddagger}$ drops to -9.2 eu for o-$CF_3C_6H_4CHClCF_2Cl$ and -8.8 eu for 2,6-$Cl_2C_6H_3CHClCF_2Cl$, and this suggests that the bulkier groups hinder the internal-return process.[21] Again the case of pentafluorobenzene is an anomaly with $\Delta S^{\ddagger}$ values around $+1$ eu and a near unity experimental isotope effect. To address this anomaly, density functional calculations were carried out to determine relative

energetics of intermediates associated with the reactions of methoxide with **I**, **II**, **9-PhFl**, and **PFB**.

Density functional B3LYP/6-31+G(d,p) calculations

Formation of both hydrogen-bonded carbanions and carbanions that are not stabilized by direct contact with an alcohol solvent molecule were proposed to explain the experimental isotope effects associated with hydron transfer between carbon and oxygen.[22] Because we were unable to obtain direct experimental evidence for the existence of these hydrogen-bonded carbanions, we decided to investigate them by calculations. The initial calculations using B3LYP/6-31+G(d,p) evaluated the stability of any possible intermediates for the reaction of $C_6H_5CH(CF_3)_2$, **I**, and CH_3O^- to $\{C_6H_5C(CF_3)_2\}^-$ [**I$^-$**] and CH_3OH, and resulted in a stable hydrogen-bonded carbanion that is 43 kcal/mol more stable than **I** and CH_3O^-, and 7 kcal/mol more stable than **I$^-$** and CH_3OH.[23] This is highly exothermic because it deals with gas-phase species and a ΔG^0_{Acid} of 375.5 kcal/mol for methanol[24] makes it a weaker acid than toluene. We continue to use B3LYP/6-31+G(d,p) and calculated values for the gas-phase acidities of **I**, **II**, **9-PhFl**, **PFB** and methanol that differ by less than 1% of the experimental values. A calculated value of $\Delta G^0_{Acid} = 333.8$ kcal/mol for the trimer $(CH_3OH)_2CH_3OH$ is similar to the ΔG^0_{Acid} for **I** and **9-PhFl**. For this reason current calculations have methanol solvating methoxide ion. Although calculations are still for gas-phase species, they mimic our experimental results for the reactions in methanol.

When the calculations use methoxide, four methanols and **II**, the transfer of charge from CH_3O^- to **II$^-$** requires 12.2 kcal/mol, Fig. 2. This energy difference is calculated using the sum of electronic and thermal free energies that result from frequency calculations that have no negative frequencies. Since calculations with six molecules are very time consuming, we tried three simplified models. Two of the models started with **II** and $CH_3O^-(HOCH_3)_3$ to give the encounter complex and CH_3OH, Fig. 3. What energy should be used for the released methanol? When the energy is calculated using a single gas-phase methanol that first step requires +3.1 kcal/mol. To approximate the energy of a solvated methanol, the energy used was one third of $(CH_3OH)_3$ and the first step now requires +5.5 kcal/mol. This would result in an overall energy going from $CH_3O^-(HOCH_3)_3$ and **II** to methanol and the hydrogen-bonded carbanion of +10.9 kcal/mol or +13.3 kcal/mole. A third model has the dimer $(CH_3OH)_2$, $CH_3O^-(HOCH_3)_3$, and **II** and would form $(CH_3OH)_3$ instead of a methanol and the encounter complex. This makes the energy for step one +7.8 kcal/mol, and increases the energy to form the hydrogen-bonded carbanion and $(CH_3OH)_3$ to +15.6 kcal/mol. Since we
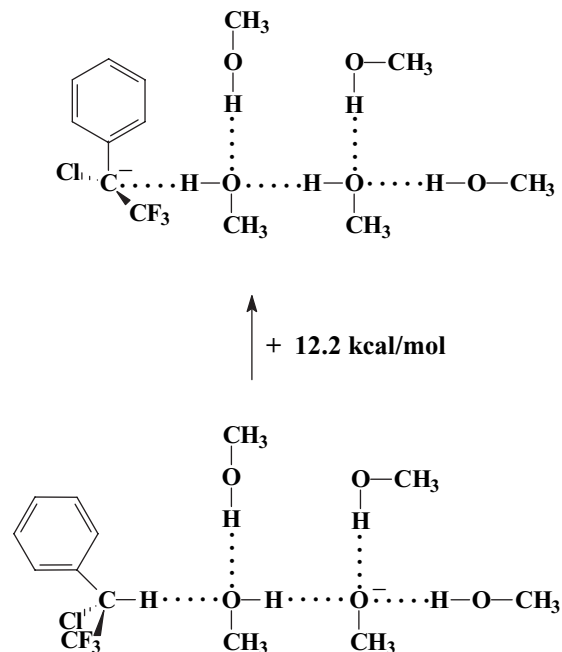
Figure 2. The energy calculated by B3LYP/6-31+G(d,p) required to transfer charge from a solvated methoxide ion to PhenylCCClCF$_3$

are only interested in comparing the relative energetics for the reactions of **II** versus **PFB**, the three models give similar results and Fig. 3 uses the value for a methanol that is one third that of $(CH_3OH)_3$.

The energy to form an encounter complex is similar for the two carbon acids. A big difference comparing **II** to **PFB** is in the energy required to form the hydrogen-bonded carbanion from the encounter complex and this is more favorable for **PFB**. On the other hand, since **II** and **PFB** have similar gas-phase acidities, the breaking of the hydrogen bond to form a free carbanion is less favorable for **PFB**. If the reactions require the formation of a free carbanion then the two compounds should result in similar rates of reaction. This cannot be the case since the reactions of **PFB** are about 66,000 times faster than those for **II**. Calculations carried out in the PCM mode using the dielectric constant of methanol do not give a better model as the last step to form the free carbanions and $(CH_3OH)_3$ becomes exothermic, and would not agree with the large amounts of internal return required to obtain the near unity experimental PKIE values. One possible explanation of the experimental results for **PFB** is that it is not necessary to form a free carbanion and exchange can occur directly from a hydrogen-bonded carbanion. This would also agree with experimental $\Delta S^\ddagger$ values of near zero obtained for the reactions of **PFB**, which are consistent with reactions occurring from hydrogen-bonded carbanions. Calculations are in progress to find out how exchange can occur directly from a hydrogen-bonded carbanion.

Results of calculations for the reactions of $CH_3O^-(HOCH_3)_3$ with **I** compared to **9-PhFl** are given

Pentafluorobenzene [PFB]
Gas Phase Acidity is 349.2 kcal and exchange in MeONa/MeOH (25 °C) has k = 2.96 x 10⁻² M⁻¹s⁻¹

C₆H₅CHClCF₃ [II]
Gas Phase Acidity is 348.7 kcal and exchange in MeONa/MeOH (25 °C) has k ~ 4.5 x 10⁻⁷ M⁻¹s⁻¹
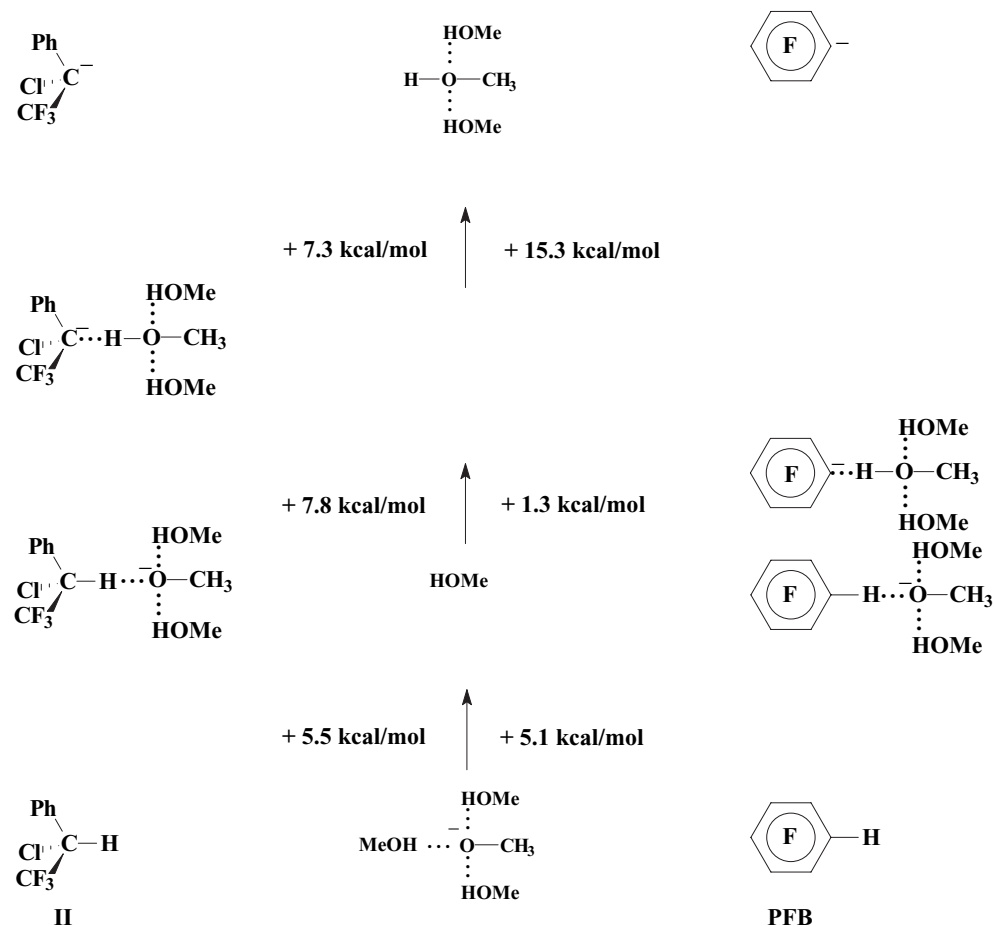
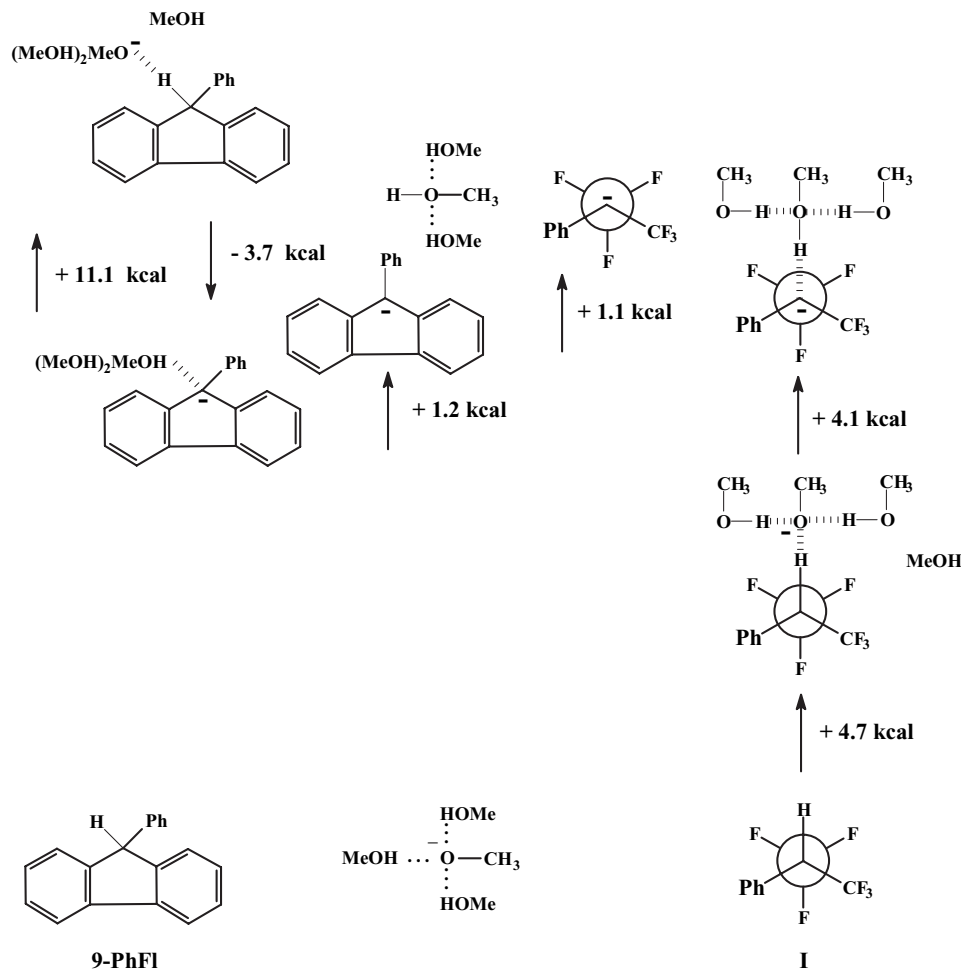**Figure 3.** Energies calculated using B3LYP/6-31+G(d,p) for **II** and **PFB**

in Fig. 4. The two compounds differ significantly from the start. The formation of the encounter complex from a reaction of **I** and $CH_3O^-(HOCH_3)_3$ is similar in energy as those from the reactions of **II** and **PFB**. The formation of the hydrogen-bonded carbanion requires less energy for **I** than for **II**, which is not unreasonable since **I** is a stronger acid than **II**. There is still the anomaly of the ease of formation for the hydrogen-bonded carbanion obtained from the reaction of **PFB**, which is a much weaker acid than **I**. The energy required for the formation of the encounter complex for **9-PhFl** is much greater than that required for the other three compounds; however, the hydrogen-bonded carbanion for **9-PhFl** is more stable than the encounter complex. This analysis agrees with the experimental PKIE and $\Delta S^{\ddagger}$ values that are consistent with only a small amount of internal return occurring during the reaction mechanism. The electrons of the negative charge for the anions of **I**, **II**, and **9-PhFl** reside in orbitals that are π-delocalized [delocalized anions] while electrons of the negative charge for **PFB⁻** would be in an sp^2 localized orbital [localized anion].

Reactivity of delocalized and localized anions

We first became aware of a difference in hydron transfer reactions occurring with delocalized and localized carbanions from our studies of the nucleophilic reactions of alkoxides with fluoroalkenes. The rapid reaction of methanolic sodium methoxide with $CF_2=CCl_2$ gives the saturated ether $CH_3OCF_2CHCl_2$ as the only product.[25] Hine et al.[26] reported the rates of methoxide-catalyzed exchange for $CDCl_2CF_3$ at 0 and 20°C and the methoxide-promoted dehydrofluorination of $CHCl_2CF_3$ at 55 and

9-Phenylfluorene [9-PhFl]
Gas Phase Acidity is 335.6 kcal and exchange in MeONa/MeOH (25 °C) has k = 1.54 x 10⁻³ M⁻¹s⁻¹

$C_6H_5CH(CF_3)_2$ **[I]**
Gas Phase Acidity is 335.3 kcal and exchange in MeONa/MeOH (25 °C) has k = 2.09 x 10⁻³ M⁻¹s⁻¹

Figure 4. Energies calculated using B3LYP/6-31+G(d,p) for **9-PhFl** and **I**

70°C. The only products isolated from the dehydrofluorination reaction were $CH_3OCF_2CHCl_2$ and $CH_3OCF=CCl_2$. The formation of the saturated ether is readily explained since the reaction of methoxide with $CF_2=CCl_2$ has a half-life of 40 min at 0°C, and the rate of the methoxide-promoted elimination of $CH_3OCF_2CHCl_2$ is twice as fast as that for $CHCl_2CF_3$. Since the rate of exchange for $CH_3OCF_2CDCl_2$ is over 7000 faster than the rate of elimination of $CH_3OCF_2CHCl_2$ at 20°C, it is not surprising that $\{CH_3OCF_2CCl_2\}^-$ generated from the reaction of methanolic methoxide and $CF_2=CCl_2$ adds a proton from methanol rather than eliminating a fluoride ion to give the vinyl ether. The two types of reaction are an excellent method to generate the same carbanion intermediate by different approaches.

Our first use of this method was the detailed study of the reactions of $C_6H_5C(CF_3)=CF_2$ with ethanolic sodium ethoxide at −78°C.[27] The carbanion intermediate, $\{C_6H_5C(CF_3)CF_2OC_2H_5\}^-$, favors elimination of fluoride ion to form both vinyl ethers, $C_6H_5C(CF_3)=CFOC_2H_5$, and only 15% of the saturated ether $C_6H_5CH(CF_3)CF_2OC_2H_5$. When the reaction is carried out in C_2H_5OD the amount of saturated ether remains almost constant at 13% and this suggests hydron transfer to the carbanion occurs with a near unity isotope effect. The ethoxide-promoted dehydrofluorination of $C_6H_5C^iH(CF_3)CF_2OCH_3$ also occurs with a near unity value for k^H/k^D at 25°C. Reaction of ethoxide with $C_6H_5CH(CF_3)CF_2OCH_3$ in C_2H_5OD results in 3–4% deuterium incorporation at 20% elimination of fluoride and this matches the partitioning of the carbanion generated from

the reaction of $C_6H_5C(CF_3)$=CF_2 with ethoxide in C_2H_5OD at 25°C.[28] Since the carbanion intermediate, $\{C_6H_5C(CF_3)CF_2OCH_3\}^-$, does not eliminate methoxide ion to generate $C_6H_5C(CF_3)$=CF_2, the reactions of alkoxides with fluoroalkenes are not reversible.

Replacing a chlorine of CF_2=CCl_2 with a phenyl, CF_2=$CClC_6H_5$, decreases the rate of reaction with methanolic sodium methoxide by a factor of four and results in a product distribution of 51% $CH_3OCF_2CHClC_6H_5$ and 49% CH_3OCF=$CClC_6H_5$.[28] This is a significant difference in the transfer of a proton from methanol to a localized carbanion, $\{CH_3OCF_2CCl_2\}^-$, compared to a delocalized carbanion, $\{CH_3OCF_2CClC_6H_5\}^-$. These results were the start of our program on proton transfer reactions. The experimentally measured gas-phase acidity of $CHCl_2CF_3$, $\Delta G^0_{Acid} = 348.2$ kcal/mol, is similar to that of $C_6H_5CHClCF_3$ [$\mathbf{II}$], $\Delta G^0_{Acid} = 348.7$ kcal/mol; however, rates of methanolic sodium methoxide exchange at 25°C differ significantly. The rate of $CDCl_2CF_3$, 1.90×10^{-2} $M^{-1}s^{-1}$, is 45,000 times faster than that for $\mathbf{II}$-d after making a correction for rates in ethanol to methanol, Fig. 1. The rate of ethoxide-promoted dehydrofluorination of $C_6H_5CHClCF_3$ at 70°C, $k = 3.69 \times 10^{-4} M^{-1}s^{-1}$,[18] when corrected for the change to methanolic sodium methoxide,[29] $k = 1.2 \times 10^{-5} M^{-1}s^{-1}$, is similar to the reported value for $CHCl_2CF_3$, $1.9 \times 10^{-5} M^{-1}s^{-1}$.[26b] The methoxide-promoted dehydrochlorination of $C_6H_5CHClCF_2Cl$, $k = 6.74 \times 10^{-4} M^{-1}s^{-1}$ at 0°C, has a two-step mechanism with chloride leaving from the hydrogen-bonded carbanion.[30] This can be compared to one at 0°C for $CHCl_2CF_2Cl$, $k = 4.4 \times 10^{-2} M^{-1}s^{-1}$. Therefore, the rates for the $C^iHCl_2CF_2X$ are faster than those for $C_6H_5C^iHClCF_2X$ by 2 for the dehydrofluorination and 66 for dehydrochlorination. The significant difference comes when comparing the rates for the hydron exchange reactions.

Differences in reactivity between delocalized and localized anions are often attributed to a greater density of charge on the reacting atom of a localized anion. However, the calculated NPA charge for the benzylic carbon of $\mathbf{II}^-$, -0.367, is only 11% smaller than the charge calculated for the ipso carbon of $\mathbf{PFB}^-$, -0.414, and 19% smaller than the charge for $\{CF_3CCl_2\}^-$, -0.453. Charge distributions for the acidic C—H bonds are also similar: $\mathbf{II}$, C $= -0.327$, H $= +0.295$; $\mathbf{PFB}$, C $= -0.355$, H $= +0.284$; $CHCl_2CF_3$, C $= -0.386$, H $= +0.304$. The stronger acid $\mathbf{I}$ has a greater calculated charge distribution for the C—H, C $= -0.433$ and H $= +0.307$, and a larger calculated charge on the benzylic carbon of $\mathbf{I}^-$, -0.516. Therefore, it is not the amount of charge on the carbanion, but it is the orbital available for the lone pair electrons.

Brauman and co-workers investigated the gas-phase ionic reactions of benzyl and methoxide ions, which have similar basicities but often have different reaction pathways.[31] Of interest to us was that they were unable to make the benzyl anion–methanol complex in the gas phase even though the methoxide–methanol complex is well documented in the gas phase. We have also been unable to observe anion–methanol complexes in the gas phase for any of the $\mathbf{Y}$-$\mathbf{I}^-$ or $\mathbf{Y}$-$\mathbf{II}^-$ anions. Brauman and Chabinyc[32] later reported the structure and energy correlations of hydrogen-bonded complexes of several acetylide anions with methanol. Mishima and co-workers reported the ΔG^0_{Acid} values of an extended series of ring-substituted phenylacetylenes and the stability of their phenyl acetylide anion complexes with methanol.[33] The gas-phase acidity of p-nitrophenyl acetylene, $\Delta G^0_{Acid} = 349.9$ kcal/mol, is close to that of $\mathbf{II}$, $\Delta G^0_{Acid} = 348.7$ kcal/mol, and the calculated charge on the terminal carbon of the p-nitrophenyl acetylide anion, -0.196, is less than that for the benzylic carbon of $\mathbf{II}^-$, -0.367. The p-nitrophenyl acetylide anion forms a stable complex with methanol in the gas phase that has a calculated complexation energy of 8.8 kcal/mol. The complex of $\mathbf{II}^-$-methanol is at an energy minima in our calculations; however, the free anion $\mathbf{II}^-$ and methanol are about a kcal/mol more stable than this complex. It is again an example of the difference between localized anions and delocalized anions.

EXPERIMENTAL

Materials and methods for analysis

All starting materials were purchased from Aldrich. Methanolic sodium methoxide was made by the reaction of sodium with anhydrous methanol. Methanol-O-d was purchased from Aldrich and used without further purification. The analysis of hydrogen, deuterium, and tritium exchange kinetics have been described recently.[14] NMR spectra were obtained on a Varian XL 300 MHZ FT-NMR. Calculations were carried out using the Gaussian 03 suite of programs, and optimized using B3LYP/6-31+G(d,P) and then submitted for frequency calculations and NBO analysis. The sum of electronic and thermal free energies was converted to the kcal/mol reported in Fig. 1. A detailed description of the method for measuring the gas-phase acidities is given in Ref. 6.

Synthesis of 9-phenylfluorenes

Synthesis of the 9-phenylfluorene compounds, $\mathbf{9}$-$\mathbf{YPhFl}$, was carried out as reported[34] by the reaction of YC_6H_4MgBr and 9-fluorenone to give the corresponding alcohol. The alcohol was refluxed with HI in acetic acid to form $\mathbf{9}$-$\mathbf{YPhFl}$. Deuterium was incorporated by reacting $\mathbf{9}$-$\mathbf{YPhFl}$ with sodium methoxide in MeOD to form

9-YPhFl-9-*d*. To incorporate tritium into the 9-position, 0.5 g of **9-YPhFl** and six drops of HOT was dissolved in 4 mL anhydrous glyme. The addition of 1 mL of 0.3 M MeONa/MeOH gave a precipitate that dissolved on heating the solution at 50°–60°C for 20 min at which time 2–3 mL conc. HCl was added. The **9-YPhFl-9-*t*** crystallized on cooling to room temperature. All compounds were recrystallized from ethanol.

Synthesis of YC$_6$H$_4$C^{i}HClCF$_3$

A three-step synthesis started with YC$_6$H$_4$MgBr and CF$_3$CO$_2$H to make the corresponding ketone.[35] The *p*-NO$_2$C$_6$H$_4$COCF$_3$ was synthesized from the reaction of methyl *p*-nitrobenzoate with (trifluoromethyl)trimethylsilane with anhydrous tetrabutylammonium fluoride [in THF] as the initiator and toluene as the solvent.[36,37] Ketones were reduced with the appropriate sodium borohydride to give the isotopically labeled alcohols, which were then converted to the chloride by a reaction with triphenylphosphine and carbon tetrachloride.[14] Yields for the formation of the ketones are normally between 50% and 70%, except for *p*-NO$_2$C$_6$H$_4$COCF$_3$ which was obtained in only 30%–50% yield. Although the yields for the last two steps were variable depending on the student, they can be carried out in 90% yield.

Synthesis of YC$_6$H$_4$C^{i}H(CF$_3$)$_2$

The synthesis of C$_6$H$_5$C(CF$_3$)=CF$_2$ has been described in the literature, and the same method was used to make the other YC$_6$H$_4$C(CF$_3$)=CF$_2$ compounds.[35] The reaction of YC$_6$H$_4$C(CF$_3$)=CF$_2$ with a threefold excess of CsF in dimethylformamide resulted in the formation of YC$_6$H$_4$CH(CF$_3$)$_2$, which was isolated by a co-distillation with water. The compound was pure enough to use in the kinetics experiments. Better than 99% incorporation of deuterium to form YC$_6$H$_4$CD(CF$_3$)$_2$ was realized when the reaction mixture was spiked with a tenfold excess of D$_2$O. The synthesis of C$_6$H$_5$CT(CF$_3$)$_2$ used an equal molar amount of HOT.

Acknowledgements

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9. Reference 4 has the values of k^D/k^T from 2.54 ± 0.11 to 2.46 ± 0.20 and k^H/k^T from 16.1 ± 0.6 to 15.9 ± 0.6. Our values come from rate constants obtained from our Arrhenius plots for all three isotopes of **9-PhFl-9-^{i}H**, see Table I.
10. The original Swain–Schaad relationship[7] $(k^H/k^T) = (k^H/k^D)^{1.442}$ becomes $(k^H/k^T) = (k^D/k^T)^{3.26}$. For hydron exchange reactions the later relationship is more useful. The Streitwieser group[8] uses 3.344 as the exponent in their treatment. We use 3.344 value for our calculations.
11. The equation for a^T is given in reference 8 p. 5099. We thank Prof. Andrew Streitwieser for supplying the equations to calculate a^H and a^D.
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