Rates of 1,5-Hydrogen Abstraction in 1,1,2,2-Tetrafluoro-*n*-pentyl and 1,1,2,2,3,3-Hexafluoro-*n*-pentyl Radicals

Alexander B. Shtarev,[†] William R. Dolbier, Jr.,*,[†] and Bruce E. Smart[‡]

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and DuPont Central Research & Development,[§] Experimental Station, Wilmington, Delaware 19880-03278

Abstract: A new competitive kinetic method to obtain the relative rates of intramolecular hydrogen abstraction versus intermolecular deuterium abstraction has been developed and used to measure the rates of the relatively slow unimolecular 1,5-hydrogen abstractions by 1,1,2,2-tetrafluoroalkyl ($XCH_2CH_2CH_2CF_2CF_2^\bullet$) and 1,1,2,2,3,3-hexafluoroalkyl ($XCH_2CH_2CF_2CF_2CF_2^\bullet$) radicals. Substituents at the site of C−H abstraction (X = $CH_3O−$, $CH_3S−$, $CH_3−$, $C_6H_5−$, $CH_3C(O)O−$) have only a moderate effect, with the rate constants for 1,5-shifts in the 10^3 s^{-1} range. Values of k_H and k_D for bimolecular hydrogen/deuterium transfer from t-BuMe$_2$SiH(D) and Me$_3$SiSiMe$_2$H(D) are reported along with measures of side-chain H transfer from the deuterated silanes.

Introduction

Bimolecular hydrogen transfer is utilized kinetically as a critical chain-transfer step in synthetically useful free radical chain processes.[1] In principle, *any* hydrogen atom source within the reaction medium, including the reactants, the H-transfer agent side chains, or the solvent, is capable of transferring an H-atom to propagating radicals. For most good chain reactions involving alkyl radicals, the rates of such competing hydrogen transfer processes are slow compared with the usual very fast propagating processes of addition, cyclization, rearrangement, or atom transfer. The reactivity of fluorinated radicals toward hydrogen abstraction is so much greater than that of alkyl radicals that it seemed prudent to evaluate and quantitate the degree of their expected enhanced rates of C−H reactivity.[2] In preliminary studies of the reaction of Et$_3$SiH with perfluoro-*n*-alkyl radicals, about 5% of the hydrogen transfer was found to come from the ethyl side chain![3] Also, in commercial polymerizations H-transfer from C−H bonds of surfactants and initiators can be the main source of polymer inhibition or low molecular weight product as a result of terminating chain transfer.[4] Hence, there is considerable scientific and practical interest in determining the rates of chain transfer to perfluoroalkyl radicals, and in developing structure−activity relationships where none currently exist.

As a first step in examining selectively the influence of structure on the rate constants of C−H abstraction, we chose to examine tetrafluoro- and hexafluoroalkyl radical systems **1** and **2**, which should undergo 1,5-hydrogen shifts quite readily, and where the substituent X (CH$_3$, CH$_3$S, CH$_3$O, AcO, and Ph)

can be varied with respect to its electronegativity and radical stabilizing ability. 1,1,2,2-Tetrafluoroalkyl radicals such as **1** have been shown to be only slightly less reactive than perfluoroalkyl radicals ($k_{rel} = 0.43$ for addition to styrene),[5] and
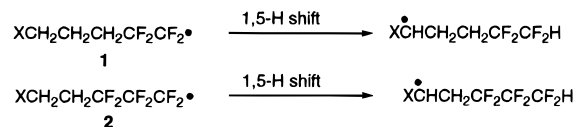
it is therefore assumed that the hexafluoro radical system **2** will have essentially "perfluoro" reactivity. The unimolecular 1,5-hydrogen shifts of **1** and **2** should have larger absolute rate constants than analogous bimolecular ones, and thus the study should be appropriate for our continued development of methodology for accurate measurement of increasingly slow processes of fluorinated radicals.[6]

1,5-Hydrogen transfer reactions from C−H bonds are quite commonly observed processes for heteroatom-centered radicals,[7] and they form the basis for name reactions such as the Barton and the Hofmann−Löfler−Freytag reactions.[8] Substituent effects on the rates and selectivity of such reactions are quite well understood.[7,9,10] In recent years, the use of 1,5-hydrogen shifts

[†] University of Florida.

[‡] DuPont Central Research and Development.

[§] Contribution No. 7819.

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Table 1. Rate Data from Competition Experiments To Determine Hydrogen Abstraction Rate Constants for Various Silanes at 25 °C

silane	slope, k_H/k_{add}[a]	intercept[a]	r^2	$k_H/10^5 M^{-1} s^{-1}$ [a]
reaction with n-C$_4$F$_9$[•] [d]				
t-BuMe$_2$SiH[b]	0.0625 ($\pm$0.003)	0.007 ($\pm$0.006)	0.998	4.9 ($\pm$0.8)
Me$_3$SiSiMe$_2$H[c]	0.400 ($\pm$0.004)	$-$0.002 ($\pm$0.002)	0.999	31 ($\pm$6)
(CF$_3$CH$_2$-CH$_2$)$_3$Si$-$H[c]	0.027 ($\pm$0.004)	0.002 ($\pm$0.016)	0.984	2.1 ($\pm$0.6)
reaction with C$_4$H$_9$-C$_2$F$_4$[•] [e]				
t-BuMe$_2$SiH[b]	0.0095 ($\pm$0.0010)	0.002 ($\pm$0.008)	0.990	1.9 ($\pm$0.4)

[a] Errors are given as 2σ. [b] Method A: Reactions were initiated with *tert*-butyl hyponitrite at 33−37 °C in BTB. [c] Method B: Reactions were UV-initiated in Pyrex tubes in 1,4-bis(trifluoromethyl)benzene at 25 °C. [d] Rate constants were determined by using the absolute rate of addition of C$_7$F$_{15}$[•] to 1-hexene obtained by lfp ($k_{add} = 7.9$ ($\pm$0.7) $\times 10^6 M^{-1} s^{-1}$ at 25 $\pm$ 2 °C).[17] [e] The rate constant was determined by using the absolute rate of addition of C$_2$H$_5$C$_2$F$_4$[•] to styrene ($k_{add} = 2.0$ ($\pm$0.1) $\times 10^7 M^{-1} s^{-1}$ at 25 $\pm$ 2 °C) obtained by lfp.[5]

of reactive (sp^2) carbon-centered radicals has become a popular method of "radical translocation",[11,12] and there is structure−reactivity data available for such reactions of vinyl radicals.[11]

Our earlier investigations of the reactivity of fluoroalkyl radicals revealed that perfluoro-*n*-alkyl radicals, probably because of similar advantageous transition state polar characteristics, have a reactivity which approaches that of *tert*-butoxyl with respect to hydrogen abstraction from *n*-Bu$_3$SnH ($k_{rel} \approx 1$) and Et$_3$SiH ($k_{rel} \approx 0.1$).[2,3] Indeed, perfluoroalkyl and tetrafluoroalkyl radicals, because of such polar factors, have much larger rate constants (M^{-1} s^{-1}) for H-abstraction from *n*-Bu$_3$SnH than do alkyl radicals: *n*-C$_8$F$_{17}$[•] 2.0 $\times$ 10^8, RCF$_2$CF$_2$[•] 9.2 $\times$ 10^7, and RCH$_2$CH$_2$[•] 2.4 $\times$ 10^6 at 25 °C.[4] Polar effects would be expected to also enhance the rates of hydrogen abstraction *from C−H bonds* by fluorinated radicals, and it was of interest to determine the relative importance of polar and thermochemical influences of substituents on such rates.

Results and Discussion

Kinetic Methodology. Within this study of intramolecular hydrogen shifts, we introduce a new kinetic method. This method was made feasible because of the significant α-deuterium isotope effect observed for the ^{19}F NMR chemical shift of a −CF$_2$H versus the analogous −CF$_2$D signal. For example, in 1,3-bis(trifluoromethyl)benzene as solvent, the signal for CH$_3$(CH$_2$)$_3$CF$_2$C*F*$_2$H (δ −136.7, d, $^2J_{FH}$ = 53.9 Hz) is baseline resolved from the signal for CH$_3$(CH$_2$)$_3$CF$_2$C*F*$_2$D (δ −137.4, t, $^2J_{FD}$ = 8.0 Hz).

Therefore, in principle, it is possible to carry out a competition between intramolecular, 1,5-H transfer to form a product with a −CF$_2$H group (i.e., **3H**) and a bimolecular D-transfer from R$_3$SiD to form a product with a −CF$_2$D group (i.e., **3D**), where the relative amounts of **3H** and **3D** provide a direct measurement of $k_{H-1,5}/k_D$. Another advantage of the use of bimolecular D-transfer is that the slower rate of such D-transfer due to the primary isotope effect allows the intramolecular 1,5-H transfer to compete more effectively.
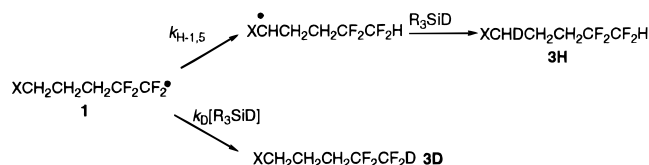
Because of the slow rates of the intramolecular H-shifts of interest, however, some of the observed XCH$_2$CH$_2$CH$_2$CF$_2$CF$_2$H (**3H**) product will inevitably derive from alternative hydrogen atom sources in the reaction medium, most specifically from the side chains of the silane reductant and from the solvent.

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Such competitive sources of H-transfer had to be quantitatively evaluated, and to the extent possible, minimized.

Choice of Solvent. The problem of competitive H-transfer from solvent in studies of slow reactions of highly fluorinated alkyl radicals can be virtually eliminated by using either 1,3- or 1,4-bis(trifluoromethyl)benzene as solvent.[6] The less expensive 1,3-isomer ("BTB") was used in these studies.

Choice of Reductant. A silane reducing agent that will give rise to minimal side chain hydrogen transfer is required. Silane (C$_2$H$_5$)$_3$SiD should have a rate constant for bimolecular D-transfer that would be sufficiently small at the concentrations required for pseudo-first-order behavior (8−10-fold excess) to allow significant competition from intramolecular 1,5-H-transfer. However, an earlier study of the importance of side chain H-transfer from (C$_2$H$_5$)$_3$SiD indicated a ratio of [R$_f$H]/[R$_f$D] = 0.13 for its reaction with *n*-C$_7$F$_{15}$[•] in benzene.[3] Similarly, ratios of 0.17−0.19 for the analogous reactions of RCF$_2$CF$_2$[•] radicals with (C$_2$H$_5$)$_3$SiD were observed. Because such large amounts of hydrogen-containing product derived from the *side chain* of the D-transfer agent are undesirable in these studies of intramolecular H-transfer, alternative D-transfer agents possessing far less propensity to donate H-atoms from their side chains were sought.

Silanes are the preferred reducing agents because of their relatively slow H-transfer rates from silicon combined with the excellent chain propagating properties of R$_3$Si[•] radicals. The silanes (CF$_3$CH$_2$CH$_2$)$_3$SiD and (cyclopropyl)$_3$SiD were chosen because of the supposed high dissociation energies of their side chain C−H bonds, but these silanes did not prove advantageous. The global value of k_H for (CF$_3$CH$_2$CH$_2$)$_3$SiH is 2.1 $\times$ 10^5 M^{-1} s^{-1} at 25 °C (Table 1), which is about 2.5 times slower than that for Et$_3$SiH and might have made it a suitable H-transfer agent.[13] Nonetheless, (CF$_3$CH$_2$CH$_2$)$_3$SiD could not be used for our studies because, quite surprisingly, *it gave more side chain H-transfer than Et$_3$SiD* ([R$_f$H]/[R$_f$D] > 1). Likewise, because (cyclopropyl)$_3$SiD yielded a [R$_f$H]/[R$_f$D] ratio slightly higher than Et$_3$SiD ([R$_f$H]/[R$_f$D] $\approx$ 0.6)), this silane also was not further pursued as a potential D-transfer agent.

Two silanes that did give lower [R$_f$H]/[R$_f$D] ratios than Et$_3$SiD were *t*-BuMe$_2$SiD ([R$_f$H]/[R$_f$D] = 0.02 and 0.07, respectively, for reaction with *n*-C$_4$F$_9$[•] and *n*-C$_4$H$_9$CF$_2$CF$_2$[•] in BTB) and Me$_3$SiSiMe$_2$D ([R$_f$H]/[R$_f$D] = 0.04 for reaction with *n*-C$_4$F$_9$[•] in BTB). These two silanes have quite different reactivities as H-transfer agents, with *t*-BuMe$_2$SiH having a global reactivity similar to that of Et$_3$SiH (k_H = 4.9 $\times$ 10^5 M^{-1} s^{-1}) and Me$_3$-

(13) Notably, this observed decrease in rate contrasts with the similar reported increase in the rate constant for H transfer to *alkyl radicals* from the "fluorous" reductant (R$_f$CH$_2$CH$_2$)$_3$SnH,[14] and this difference undoubtedly reflects the opposite nature of polar influences for H abstractions by R$_f$[•] (electrophilic) versus R[•] (nucleophilic). The proximity of the three CF$_3$ groups in (CF$_3$CH$_2$CH$_2$)$_3$SiH is apparently sufficient to have a detrimental impact on the expected polar R$_f^{\delta-}$···H···Si$^{\delta+}$ transition state.

Table 2. Rates of Hydrogen and Deuterium Abstraction by Fluorinated Radicals from Silanes in 1,3-Bis(trifluoromethyl)benzene at 25 ± 2 °C. Kinetic Isotope Effects

silane	$k_H/M^{-1} s^{-1}$ [a]	slope, k_H/k_D [a]	$k_D/M^{-1} s^{-1}$ [a]	intercept[a]
reaction with $C_4F_9{}^{\bullet}$ [b]				
$Me_3SiSiMe_2-X$	3.1 (±0.6) × 10⁶	2.42 ± 0.24	1.3 (±0.4) × 10⁶	0.10 ± 0.16
$t\text{-}BuMe_2Si-X$	4.9 (±0.8) × 10⁵	3.31 ± 0.14	1.49 (±0.30) × 10⁵	0.08 ± 0.10
reaction with $C_4H_9CF_2CF_2{}^{\bullet}$				
$t\text{-}BuMe_2Si-X$ [c]	1.9 (±0.4) × 10⁵	3.45 ± 0.10	5.5 (±1.3) × 10⁴	0.01 ± 0.08

[a] Errors are given as 2σ. [b] UV initiated in quartz at 25 °C. [c] Reaction was initiated at 35 °C with *tert*-butyl hyponitrite.

SiSiMe₂H being considerably more reactive ($k_H = 3.1 \times 10^6$ $M^{-1} s^{-1}$), as expected.[15]

In lieu of using very expensive perdeuteriosilane reducing agents, it was decided to use $t\text{-}BuMe_2SiD$, with its lower H-transfer rate constant, as the bimolecular D-transfer agent for our competition studies designed to look at unimolecular 1,5-hydrogen transfer, and to correct for any side-chain transfer (vide infra).

Determination of k_H Values of Silanes. The values of bimolecular hydrogen atom transfer, k_H, were determined for the reaction of $n\text{-}C_4F_9{}^{\bullet}$ with three silanes [$(CF_3CH_2CH_2)_3SiH$, $t\text{-}BuMe_2SiH$, and $Me_3SiSiMe_2H$] by means of kinetic competition experiments utilizing the competition between H-abstraction from the silane versus addition of the radical to 1-hexene as depicted in the scheme below.
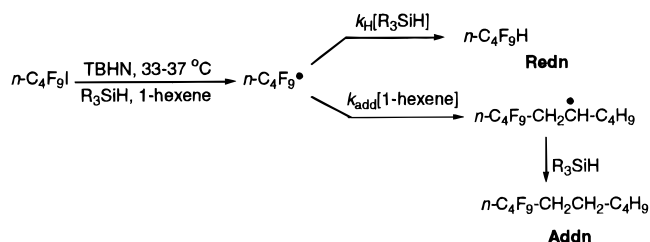
Reactions were initiated thermally by di-*tert*-butylhyponitrite ($t\text{-}Bu-O-N{=}N-O-t\text{-}Bu$) (TBHN) at 33–37 °C in BTB,[16] or by photoinitiation at 25 ± 2 °C. For each silane, the ratios of reduced product [Redn] to addition product [Addn] were obtained for a series of runs using increasing ratios of $[R_3SiH]/[1\text{-hexene}]$ with large excesses of both R_3SiH and 1-hexene being used to maintain pseudo-first-order conditions. A constant concentration of 1-hexene was maintained so that H-transfer from alkene would not contribute significantly to the slope, *but only to the intercept*. A plot of the experimental values of [Redn]/[Addn] versus $[R_3SiH]/[1\text{-hexene}]$, according to the equation below, gave straight lines, the slopes of which were equivalent to the ratios of k_H/k_{add}.

$$[\text{Redn}]/[\text{Addn}] = k_H/k_{add} \times [R_3SiH]/[1\text{-hexene}] + k_{H \text{ (from 1-hexene)}}/k_{add}$$

The value of k_{add} was taken to be that of addition of $n\text{-}C_7F_{15}{}^{\bullet}$ to 1-hexene (7.9 ± 0.7 × 10⁶ $M^{-1} s^{-1}$ at 25 ± 2 °C) which had been determined by laser flash photolysis (lfp).[5,17] The derived rate constants for hydrogen abstraction (k_H) are given in Table 1. These rate constants, as well as all other rate constants in this paper which are derived from competition studies, are reported in the tables at a temperature of 25 ± 2 °C, which is

the temperature of all of the rate constants which have been derived from laser flash photolysis.[5,17] As will be described in greater detail in the intramolecular competition section below, the slopes obtained in these competition studies exhibit *no variation between the temperatures of 25–45 °C, within experimental error. Therefore a slope (k_H/k_{add}) obtained at 45 °C can be used with a k_{add} obtained by lfp at 25 °C to obtain a value for k_H at 25 °C.*

The rate constant for hydrogen abstraction from $t\text{-}BuMe_2$-SiH by a tetrafluoroalkyl radical was determined by means of a similar competition experiment with 1-bromo-1,1,2,2-tetrafluorohexane as the substrate and styrene as the alkene. Again, the value of k_{add} for addition of $CH_3CH_2CF_2CF_2{}^{\bullet}$ to styrene had been determined by lfp [$k_{add} = 2.0 (\pm0.1) \times 10^7 M^{-1} s^{-1}$].[5]

The values of k_H that were obtained from the slope are, of course, *global* rate constants, meaning that they are the sum of rate constants for H-transfer from R_3SiH, *including from the side chain*. However, combining the values for $k_{H \text{ side chain}}/k_D$ discussed earlier with the k_H/k_D values in Table 2 shows that side chain transfer can be *ignored* because it is negligible within the error limits (0.6%, 1.7%, and 2% for $t\text{-}BuMe_2SiH/n\text{-}C_4F_9{}^{\bullet}$, $Me_3SiSiMe_2H/n\text{-}C_4F_9{}^{\bullet}$, and $t\text{-}BuMe_2SiH/RCF_2CF_2{}^{\bullet}$, respectively). Therefore, the k_H values in Table 2 will be taken to be the values for Si—H transfer.

Determination of k_D Values of Silanes. Kinetic Isotope Effects. The kinetic deuterium isotope effects (k_H/k_D) for the reactions of $n\text{-}C_4F_9{}^{\bullet}$ with R_3SiD versus R_3SiH were determined for the two silanes, $t\text{-}BuMe_2SiD$ ($k_H/k_D = 3.31 \pm 0.14$) and $Me_3SiSiMe_2D$ ($k_H/k_D = 2.4 \pm 0.3$), via a series of competition experiments in which $n\text{-}C_4F_9I$ was allowed to react with varying ratios of $[R_3SiH]/[R_3SiD]$ in BTB. The ratios of hydrogen-containing product ($n\text{-}C_4F_9H$) versus deuterium-containing product ($n\text{-}C_4F_9D$) were obtained for each run from ¹⁹F NMR spectra of the product mixture, and plots of $[n\text{-}C_4F_9H]/[n\text{-}C_4F_9D]$ versus $[R_3SiH]/[R_3SiD]$ gave a slope that equaled $k_H k_D$. By maintaining the total concentration of $R_3SiH + R_3SiD$ constant, one can be sure that hydrogen abstraction from the side chains of the silanes does not contribute to the slope, but only to the intercept value, according to the equation below. The intercept values that were obtained (Table 2) are consistent with expectations based on the evaluation of side chain reactivity discussed earlier.

$$[n\text{-}C_4F_9H]/[n\text{-}C_4F_9D] = k_H/k_D \times [R_3SiH]/[R_3SiD] + k_{H-\text{side chain}}/k_D$$

Similarly, the k_H/k_D value for the reaction of the tetrafluoroalkyl radical, $n\text{-}C_4H_9CF_2CF_2{}^{\bullet}$, with $t\text{-}BuMe_2SiH(D)$ was determined to be 3.45 ± 0.10.

With k_H/k_D values and k_H values now obtained, the values for k_D in Table 2 were calculated. It is these values of k_D for $t\text{-}BuMe_2SiD$ with $RCF_2CF_2{}^{\bullet}$ [$k_D = 5.5 (\pm1.3) \times 10^4 M^{-1} s^{-1}$] and with $n\text{-}C_4F_9{}^{\bullet}$ [$k_D = 1.45 (\pm0.30) \times 10^5 M^{-1} s^{-1}$] which will be used in the intramolecular competition studies to be described below.

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Table 3. Kinetic Data for the 1,5-H vs Intermolecular-D Transfer Studies of Tetrafluoroalkyl Radicals, **1a−d,f**,[a] and the Hexafluoroalkyl Radical, **2a**[a]

entry[a]	radical[b]	X	slope[c]	intercept[c]	$k_{H-1,5}/10^3$ s^{-1} [c]
1	**1a**	CH$_3$O−	0.070 (±0.006)	0.011 (±0.008)	3.9 (±1.3)
2[d]	**1a**	CH$_3$O−	0.068 (±0.010)	0.012 (±0.016)	
3[e]	**1a**	CH$_3$O−	0.072 (±0.006)	0.032 (±0.012)	
4[f]	**1a**	CH$_3$O−	0.053 (±0.004)	0.013 (±0.008)	2.9 (±1.0)
5	**1b**	Ph−	0.115 (0.014)	0.007 (±0.034)	6.3 (±2.3)
6	**1c**	CH$_3$COO−	0.008 (±0.0012)	0.027 (±0.002)	0.44 (±0.17)
7	**1d**	CH$_3$S−	0.063 (±0.006)	0.052 (±0.012)	3.5 (±1.2)
8	**1f**[g]	CH$_3$−	0.023 (±0.002)	0.029 (±0.004)	1.3 (±0.4)
9	**2a**	CH$_3$O−	0.046 (±0.004)	0.013 (±0.010)	6.8 (±1.5)

[a] Reactions were initiated with *trans*-bis(*tert*-butyl)hyponitrite (TBHN) in 1,3-bis(trifluoromethyl)benzene at 33−37 °C unless otherwise noted. [b] Procedures for preparation of precursor halides, **4a−e** and **5a,b**, are described in the Supporting Information. [c] Errors are reported as 2σ. [d] The reaction was done at 45 °C. [e] Initiated by UV, in quartz. [f] The reaction was done in CD$_3$COOD. [g] Precursor **4f** was prepared as described in ref 5.

Table 4. Summary of Rate Data for 1,5-Hydrogen Shifts of Tetrafluoroalkyl Radicals, **1a−d,f**, and Hexafluoroalkyl Radical, **2a**, at 25 °C

radical	X	$k_{H-1,5}/10^3$ s^{-1} [a]	$k_{H-1,5\ per\ H}/10^3$ s^{-1} [a]	k_{rel}	RSE[b]	s_p[c]	s^+ [c]
1a	CH$_3$O−	3.9 (±1.3)	1.95 (±0.70)	3	5.3	−0.27	−0.78
1b	Ph−	6.7 (±2.3)	3.3 (±1.2)	5	7.8[d]	−0.01	−0.18
1c	CH$_3$COO−	0.44 (±0.17)	0.22 (±0.09)	0.3	2.4[e]	+0.31	−0.19
1d	CH$_3$S−	3.5 (±1.2)	1.75 (±0.6)	2.7	5.6	−0.00	−0.60
1f	CH$_3$−	1.3 (±0.4)	0.65 (±0.2)	1	3.3	−0.17	−0.31
2a	CH$_3$O−	6.8 (±1.5)	3.4 (±0.8)		5.3	−0.27	−0.78

[a] Errors are given as 2σ. [b] Reference 22. [c] Reference 23. [d] The value given is that calculated for CH$_2$=CH−. [e] The value given is that calculated for the formate group.

Intramolecular 1,5-Hydrogen Abstraction Rate Constants. Rates of intramolecular hydrogen abstraction were determined by competition experiments where the unimolecular 1,5-hydrogen shifts of 1,1,2,2-tetrafluoropentyl radicals (**1**) were allowed to compete with their bimolecular abstraction of deuterium from *t*-BuMe$_2$SiD (Table 3).
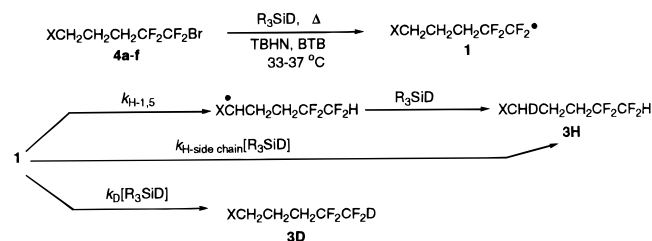
The small residual side chain H-transfer ($k_{H-side\ chain}$) from *t*-BuMe$_2$SiD should be reflected by the intercept of the plot of [R$_f$H]/[R$_f$D] versus 1/[*t*-BuMe$_2$SiD], with the slope providing unambiguously the ratio of $k_{H-1,5}/k_D$. (Any bimolecular H-transfer from the substrate would have an impact only on the intercept since *constant* concentrations of the substrate were used in kinetic studies.)

Indeed, good straight lines were obtained for the plot of [**3H**]/[**3D**] versus 1/[*t*-BuMe$_2$SiD]. The intercept values were small and, within experimental error, consistent with the $k_{H-side\ chain}/k_D$ values (0.02−0.07) that were obtained from control experiments that examined the degree of side chain H-transfer in the reaction of tetrafluoroalkyl bromide derivatives with *t*-BuMe$_2$-SiD.[18]

$$\frac{[3H]}{[3D]} = \frac{k_{H-1,5}[1] + k_{H-side\ chain}[1][R_3SiD]}{k_D[1][R_3SiD]} = \frac{k_{H-1,5}}{k_D[R_3SiD]} + \frac{k_{H-side\ chain}}{k_D}$$

Temperature Dependence of Slope. As mentioned earlier, and as seen from the data in Table 3, the slopes at 35° and at 45° are virtually indistinguishable. Since it can be assumed that

the slope at 25° also would be the same, it is therefore legitimate to use k_{add} values which were obtained in lfp experiments at 25 °C to calculate $k_{H-1,5}$ values at 25 °C, using the competition data obtained at 33−38 °C.

Substituent Effects on Rate Constants. From the data in Table 4 the order of reactivities is Ph > OCH$_3$ ≈ SCH$_3$ > CH$_3$ > OAc, which correlates reasonably well with the relative abilities of the substituents to stabilize free radicals,[19] but even though they do not correlate as well, transition state polar interactions cannot be ruled out. In all likelihood, both factors contribute to the observed trend.[20]

The smaller slope (0.053) observed for **1a** when the competition is carried out in perdeuterio acetic acid (Table 3) is consistent with the transition state for D-abstraction from the silane having more polar character than that for the 1,5-H abstraction from carbon. Therefore, k_D should be affected more than $k_{H-1,5}$ when one switches from BTB to the much more polar solvent, acetic acid.

The *range* of observed reactivities for the series of tetrafluoroalkyl radicals **1a−d,f** is quite narrow, with phenyl[24] and methoxy substituents increasing the rate of hydrogen abstraction over that of an ordinary secondary C−H only by factors of 5 and 3, respectively.[25] This range of reactivities is comparable

(18) The results of these competition experiments are very reproducible from run to run, with similar slopes being obtained even when one does not use absolutely fresh silane.

(19) Fischer, H. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyi, R., Eds.; Reidel: Dordrecht, 1986; pp 123−142.

(20) The rate for 1,5-hydrogen shift in the hexyl radical (CH$_3$(CH$_2$)$_4$-CH$^•$ in the gas phase at 25 °C (7−15 s^{-1})[21] is about 2 orders of magnitude slower than that for **1f**, which likely reflects a favorable polar effect in the transition state for hydrogen shift in **1f**.

(21) (a) Watkins, K. W. *J. Phys. Chem.* **1973**, *77*, 2938. (b) Dóbé, S.; Bérces, T.; Réti, F.; Márta, F. *Int. J. Chem. Kinet.* **1987**, *19*, 895.

(22) (a) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062. (b) Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623. (c) Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Rüchardt, C. *J. Org. Chem.* **1998**, *63*, 1935.

(23) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(24) The competition of intramolecular versus intermolecular hydrogen abstraction for phenyl derivative was accompanied by a lower yield of the reduced products. The reason for that was an observed competitive intramolecular cyclization of the fluorinated radical onto the aromatic ring to form a tetrahydonaphthalene product, a process that will be discussed in more detail in a subsequent publication. The overall mass balance remained excellent.

to that observed by Curran and Shen for substituent effects in 1,5-hydrogen migrations of vinyl radical **6**.[11] Because their study was run at 80 °C, versus this work at 25 °C, it is unfortunately not possible to directly compare absolute rate constants for the two studies. The compact range of reactivities for both our
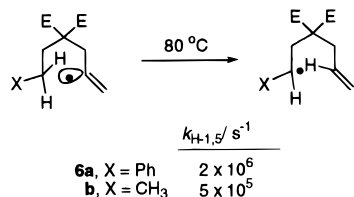
system and that of Curran is consistent with low activation energy, high entropic-demand processes, which therefore should exhibit little substituent-based selectivity.

It is interesting to compare the unimolecular rates for 1,5-H shift of methoxy-substituted radical **2a** [3.4 ($\pm$0.8) $\times$ 10^3 s^{-1}] with a preliminary value recently obtained for *bimolecular* abstraction by n-C$_4$F$_9^{\bullet}$ from the CH$_2$ groups of diethyl ether [$k_{\text{H per hydrogen}}$ = 5.5 ($\pm$1.2) $\times$ 10^3 M^{-1} s^{-1}].[26] The rate constants are very similar, suggesting similar activation parameters for the intra- and intermolecular reactions. It should be noted that because of the *concentration dependence* of the bimolecular rate, the *observed* rate for bimolecular C–H abstraction by n-C$_4$F$_9^{\bullet}$ could be faster or slower than the unimolecular rate of **2a** depending on the concentration of the organic substrate.

Hexafluoro- versus Tetrafluoroalkyl Radicals. The greater reactivity observed for hexafluoroalkyl radical **2a** (a factor of 1.7 times faster than **1a**) is consistent with the general observation that such radicals are "perfluoro-like" and thus somewhat more electrophilic and reactive than the analogous tetrafluoroalkyl radicals. For example, the CH$_2$=CHCH$_2$CF$_2$-CF$_2$CF$_2^{\bullet}$ undergoes 5-*exo*-cyclization 3.9 times faster than CH$_2$=CHCH$_2$CH$_2$CF$_2$CF$_2^{\bullet}$ and abstracts H from n-Bu$_3$SnH 2.2 times faster.[5,27]

Conclusions

The most important conclusion from this work is that techniques have been devised to obtain an accurate and reliable measure of the rate constants of the relatively slow 1,5-hydrogen transfer processes of fluorinated radicals in solution. Very few absolute rate constants have been previously reported for intramolecular hydrogen transfer processes in solution.

The results indicate a reasonable, but rather compressed impact of substituents at the site of C–H abstraction. The rate constants of these 1,5-shifts are in the 10^3 s^{-1} range, and although such processes are likely much faster than those of the analogous hydrocarbon radicals, they are not nearly fast enough to be competitive with the 6-*exo*-heptenyl cyclization reactions of fluorinated alkenes, which have been observed to proceed with rate constants of >10^7 s^{-1}.[28] As observed earlier by Curran and Shen for 1,5-hydrogen shift processes of vinyl radicals,[11] the rates of intramolecular, 1,5-hydrogen transfer for tetrafluoro- and hexafluoroalkyl radicals appear to be of a similar magnitude to their analogous bimolecular rates for C–H abstraction.

(25) Dimethylamino-substituted substrates, **4d** and **5b**, did not undergo the kind of clean free radical chain processes which would allow reliable rate data to be obtained.

(26) Shtarev, A. B.; Dolbier, W. R., Jr.; Smart, B. E. Unpublished results.

(27) Dolbier, W. R., Jr.; Rong, X. X.; Bartberger, M. D.; Koroniak, H.; Smart, B. E.; Yang, Z.-Y. *J. Chem. Soc., Perkin Trans. 2* **1998**, 219.

(28) Dolbier, W. R., Jr.; Li, A.; Smart, B. E.; Yang, Z.-Y. *J. Org. Chem.* **1998**, *63*, 5687–5688.

Experimental Section

General. ^{1}H NMR (CDCl$_3$, TMS internal reference) and ^{19}F NMR (CDCl$_3$, CFCl$_3$ internal reference, δ negative upfield) spectra were recorded at 300 and 282.33 MHz, respectively, on a Varian VXR-300 spectrometer unless otherwise indicated. UV spectra were recorded on an HP8452A UV/VIS spectrometer.

Synthetic procedures for all substrates used in the kinetic studies can be found in the Supporting Information.

Competition Kinetics. The competition kinetic reactions were done in 1,3-bis(trifluoromethyl)benzene (BTB) as a solvent if not otherwise stated.

General Procedure for the Competition Experiment of Hydrogen Abstraction from Silanes versus Addition to Olefins. Each NMR tube of the series, provided with a capillary glass tube containing a solution of CFCl$_3$ in C$_6$D$_6$ as an external standard for measuring ^{19}F NMR, was flushed with nitrogen. Into each tube a known volume of the solvent was added. The concentration of the reactants was determined according to weight ($\pm$0.001 g), the volume of silane was varied, and the concentration of other reagents was kept constant through the series of tubes (Method A). The concentrations of both the silane and olefin were changed in Method B. Each tube was sealed with a rubber septum, secured with Parafilm tape, frozen in liquid nitrogen, and subjected to three successive freeze–pump–thaw cycles followed by pressurization with nitrogen and warming up to room temperature. The tubes were then subjected to UV photolysis in a Rayonet reactor at room temperature for the UV-initiated reactions, or were done at 33.5–37.5 °C in the presence of di-*tert*-butylhyponitrite[16] as a radical initiator for the thermally initiated reactions until the sufficient consumption of starting material was determined by ^{19}F NMR. Product ratios for the various concentrations of silane and olefin allowed the determination of the $k_{\text{H}}/k_{\text{add}}$ ratio. Yields were determined by integration of product signals versus the resonance of CFCl$_3$.

See the Supporting Information for detailed information about specific competition studies, along with tables of kinetic data (Tables 5–7).

General Procedure for the Competition between Hydrogen Abstraction from R$_3$SiH and Deuterium Abstraction from R$_3$SiD. Much as described above, reactions were carried out in BTB solvent and were initiated by either UV-irradiation in quartz tubes or thermally at 35 °C with di-*tert*-butylhyponitrite as initiator. Keeping the total concentration of silanes constant, the ratio of [R$_3$SiH]/[R$_3$SiD] was varied within each series, and the ratios of [R$_{\text{HF}}$H]/[R$_{\text{HF}}$D] were determined by integration of the –CF$_2$H and –CF$_2$D signals in the ^{19}F NMR (δ –136.7 versus –137.4, respectively).

See the Supporting Information for detailed information about specific competition experiments, along with tables of kinetic data (Tables 8–10).

General Procedure for Competition of Intramolecular, 1,5-H Abstraction versus Intermolecular Deuterium Abstraction from t-BuMe$_2$SiD for 1,1,2,2-Tetrafluoropentyl Radicals 1a–d,f and 1,1,2,2,3,3,-Hexafluoropentyl Radical 2a. The reactions were carried out at 35 °C with di-*tert*-butylhyponitrite as initiator. Ratios of n-R$_{\text{HF}}$H/ n-R$_{\text{HF}}$D for intramolecular hydrogen abstraction versus intermolecular deuterium abstraction from *tert*-butyldimethylsilane-*d* were determined by integration of the –CF$_2$H δ_{F} –137 (d, J = 54 Hz) and –CF$_2$D, δ_{F} –137.7 (t, J = 8 Hz) resonances in the ^{19}F NMR of the tetrafluoroalkyl products, and the signals at CF$_2$H δ –138.8 (d, J = 54 Hz) and CF$_2$D δ –139.5 (t, J = 8 Hz) resonances in the ^{19}F NMR of the hexafluoroalkyl product.

Supporting Information Available: Procedures for synthesis of substrates, **4a**–**e** and **5a**–**b**, specific procedures for competition experiments, and tables of kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.