

Absolute Rates of Intermolecular Carbon–Hydrogen Abstraction Reactions by Fluorinated Radicals[§]

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Abstract: Using competition kinetic methodology, absolute rate constants for bimolecular hydrogen abstraction from a variety of organic substrates in solution have been obtained for the n -C₄H₉CF₂CF₂[•], n -C₄F₉[•], and i -C₃F₇[•] radicals. Fluorine substitution substantially increases the reactivity of alkyl radicals with respect to C–H abstraction, with the secondary radical being most reactive. A wide range of substrate reactivities (5200-fold) was observed, with the results being discussed in terms of an interplay of thermodynamic, polar, steric, stereoelectronic, and electrostatic/field effects on the various C–H abstraction transition states. Representative carbon–hydrogen bond dissociation energies of a number of ethers and alcohols have been calculated using DFT methodology.

Introduction

Perfluoroalkyl radicals have exceptional reactivity characteristics that derive largely from their great electrophilicity but also somewhat from their pyramidal nature.¹ Thus rate constants for hydrogen abstraction by perfluoroalkyl radicals from relatively electropositive atoms such as Sn, Si, or even carbon are much larger than those of the analogous alkyl radicals. For example, the rate constants for hydrogen abstraction from n -Bu₃SnH and Et₃SiH by n -R_f[•] are 85 and 714 times larger, respectively, than by n -R[•].^{2–4} With a preliminary indication of molar rate constants in the range of 10⁴–10⁵ M⁻¹ s⁻¹ for hydrogen transfer from relatively good C–H donors such as tetrahydrofuran (THF),¹ we considered it important to evaluate and quantitate the bimolecular C–H donor ability of a broad range of functionalized organic compounds having C–H bonds in a variety of molecular environments. 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.⁵ 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.

It has been demonstrated elegantly in studies mostly of the t -BuO[•] radical, by Beckwith,^{6,7} Ingold,⁸ Scaiano,⁹ Wong,¹⁰ Roberts,¹¹ and Critch,¹² and in Walling's earlier studies of both t -BuO[•] and Cl[•],¹³ that in the bimolecular abstraction of a

hydrogen atom from organic substrates, steric, thermochemical, polar, and stereoelectronic effects can all play significant roles in determining both the site of greatest reactivity and the rate constant of hydrogen abstraction from this site.

All other things being equal, the most weakly bound C–H bond will generally undergo H-abstraction. It has been demonstrated that in many radical substitution reactions there is a direct relationship between the energy of activation and the bond strength of the bond being broken (Evans–Polanyi equation: $E_a = \alpha[D_{R-H}] + \text{constant}$).¹⁴ For abstractions of hydrogen from stannanes, germanes, and silanes, good correlations have been observed, with α -values for n -alkyl[•], perfluoro- n -alkyl[•], and t -BuO[•] radicals of 0.50, 0.34 and 0.22, respectively, the trend being an indication of greater reactivity along the series.^{15,16}

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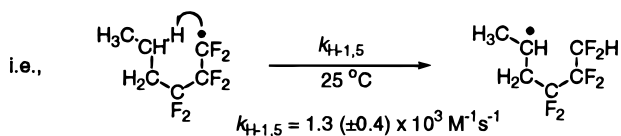
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Scheme 1



The importance of polar influences in H-abstraction processes has been demonstrated, for example, by the observation that butyrolactone undergoes H-abstraction by *t*-BuO[•] exclusively at the γ -position, adjacent to the ether oxygen,^{6b} whereas, in contrast, Roberts has shown that the α -hydrogen is exclusively removed when the reverse-polarity boryl radical, R₃N[•]→BHR[•] is used.¹¹

Prior to initiating the current study of bimolecular C–H abstraction reactivity, a more limited examination of intramolecular, 1,5-hydrogen shift processes of fluorinated alkyl radicals of the general type XCH₂CH₂CF₂CF₂CF₂[•] and XCH₂CH₂CH₂CF₂CF₂[•], where X = CH₃, OCH₃, SCH₃, and Ph, was first carried out.¹⁷

In this study it was confirmed that, although slow by comparison to other reactions of fluorinated radicals (such as very fast 5-*exo*-hexenyl and 6-*exo*-heptenyl cyclizations, bimolecular alkene additions, or H-abstractions from R₃SiH or R₃SnH reductants), the rate constants for such 1,5-H transfer were in the 10³–10⁴ M⁻¹ s⁻¹ range. Such rate constants were much larger than those for comparable H-transfers of purely hydrocarbon radicals (Scheme 1).¹⁸

An important attained goal of this study of intramolecular H-transfer was our ability to demonstrate the efficacy of a new competitive method designed to obtain rate constants of relatively slow H-transfer processes via competitive D- versus H-transfer. The desired rate constants were obtained by means of a competition between the intramolecular C–H transfer and a bimolecular transfer of *deuterium* from *t*-BuMe₂SiD, the rate constant of which was a relatively slow 1.49 (±0.3) × 10⁵ M⁻¹ s⁻¹ for abstraction by *n*-C₄F₉[•].¹⁷ This new competitive method was made possible by the fact that the ¹⁹F signals for *n*-CF₃CF₂CF₂CF₂-H and *n*-CF₃CF₂CF₂CF₂-D are separated by 0.7 ppm and are fully resolved, thus allowing a simple integration of the signals to provide the relative concentrations of the two products.¹⁷

In the present study, we have examined the competition between two *bimolecular* processes, the transfer of hydrogen from the organic substrate versus the transfer of deuterium from *t*-BuMe₂SiD, under thermal initiation using *tert*-butylhyponitrite (TBHN) in 1,3-bis(trifluoromethyl)benzene (BTB) as solvent, as shown in Scheme 2.

For each substrate the ratios [n-C₄F₉H]/[n-C₄F₉D] were obtained for a series of runs where the ratio of [substrate]/[*t*-BuMe₂SiD] was varied, while maintaining [*t*-BuMe₂SiD] constant. Under these conditions, plots of [n-C₄F₉H]/[n-C₄F₉D] versus [substrate]/[*t*-BuMe₂SiD] resulted in straight lines, the slopes of which equaled $k_{\text{H}}/k_{\text{D}}$, with the intercepts being a measure of the constant amount of side chain H-transfer from *t*-BuMe₂SiD, as indicated in eq 1.

$$\frac{[n\text{-C}_4\text{F}_9\text{H}]/[n\text{-C}_4\text{F}_9\text{D}]}{k_{\text{H}}/k_{\text{D}} \times [\text{substrate}]/[t\text{-BuMe}_2\text{SiD}] + k_{\text{H-side chain}}/k_{\text{D}}} \quad (1)$$

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Results and Discussion

The organic substrates used in this initial investigation were chosen on the basis of two main criteria: (a) structural simplicity, that is molecules having a minimum of different C–H bonds, and (b) to provide a reasonable variety of structural (functional group) types. The following molecules chosen for study. *Alkanes*: cyclohexane, cyclopentane, and *n*-heptane. *Aromatic hydrocarbons*: mesitylene and cumene. *Haloalkanes*: 1,2-dichloroethane and 1-chlorohexane. *Ethers*: tetrahydrofuran, tetrahydropyran, 1,4-dioxane, 1,3-dioxolane, 2,2-dimethyl-1,3-dioxolane, 1,3,5-trioxane, diethyl ether, dimethyl ether, dimethoxymethane, and dimethoxyethane. *Thioether*: tetrahydrothiophene. *Alcohols*: methanol, 2-propanol, and 2,3-dihydroxybutane.

Three types of fluorinated radicals were examined: the less reactive tetrafluoroalkyl radical, *n*-C₄H₉CF₂CF₂[•], the standard straight chain perfluorinated radical, *n*-C₄F₉[•], and the more reactive secondary perfluorinated radical, (CF₃)₂CF[•]. The broadest study was that of *n*-C₄F₉[•], with the other two being examined primarily for comparison purposes.

(1) Rate Constants for *t*-BuMe₂Si-D Transfers. To carry out the desired competition experiments, it was necessary for us to know the rate constants for deuterium transfer from *t*-BuMe₂SiD for each of the three fluorinated radicals. Two of these, those for RCF₂CF₂[•] and *n*-C₄F₉[•], were reported in the preceding publication in this series on intramolecular C–H transfer, which served to introduce this competition kinetic technique.¹⁷ The rate constant for D-abstraction from *t*-BuMe₂SiD by the *i*-C₃F₇[•] radical was obtained by first obtaining the value for k_{H} utilizing the competition between its addition to pentafluorostyrene and its abstraction of H from *t*-BuMe₂SiH. This value of k_{H} , combined with data from competitive H- and D-abstraction from *t*-BuMe₂SiH and *t*-BuMe₂SiD, provided the kinetic data given in Table 1.

Nothing startling can be found among the data in Table 1. As would be expected, (a) the more electronegative the radical, the *more* reactive it is toward abstraction of H/D from the electropositive silicon atom, and (b) the more reactive the radical the *less* selective it is in abstraction of H versus D.

(2) Bimolecular C–H Abstraction Rate Constants. As indicated above, the substrate C–H donors were chosen in order to obtain as much insight as possible regarding C–H structure–reactivity relationships. Table 2 presents the data that were obtained from the competition experiments, using the three fluorinated radicals with the various organic substrates.

There is a considerable range (5200-fold) in the rate constants observed, from a low of 1.5 × 10¹ M⁻¹ s⁻¹ per H for the reaction of *n*-C₄F₉[•] with 1,2-dichloroethane to a high of 7.8 × 10⁴ M⁻¹ s⁻¹ per α -H for the reaction of *i*-C₃F₇[•] with THF. Even when considering reactions within only one class of radical, a reasonably large range of reactivities (590-fold) is exhibited by the *n*-C₄F₉[•] radical. For the purpose of comparison, it can be useful to “normalize” the molecular rate constants in Table 2 to take into account the different numbers of reactive hydrogen atoms present in each molecule, with these values being given in the last column.²⁰

(18) For example, using activation parameters reported for the 1,5-H shift rearrangement of the 1-hexyl to the 2-hexyl radical (log *A* = 9.5 and *E_a* = 11.6 kcal/mol),¹⁹ the rate constant of this hydrocarbon radical rearrangement ($k_{1,5\text{-H}}$ = 9.6 s⁻¹) is ~2 orders of magnitude smaller than that for the analogous rearrangement of tetrafluorohexyl radical, CH₃CH₂CH₂CH₂CF₂CF₂[•] ($k_{1,5\text{-H}}$ = 1.3 × 10³ s⁻¹).¹⁷

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Scheme 2

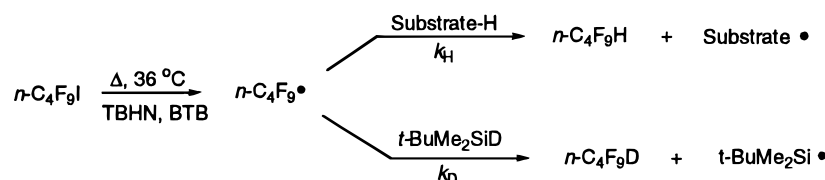


Table 1. H- and D-Abstraction Rate Constants from *t*-BuMe₂SiH(D) by *n*-C₄H₉CF₂CF₂•, *n*-C₄F₉•, and *i*-C₃F₇• Radicals at 25 ± 2 °C

radical	rate constants, M ⁻¹ s ⁻¹		
	<i>n</i> -C ₄ H ₉ CF ₂ CF ₂ • ^a	<i>n</i> -C ₄ F ₉ • ^a	<i>i</i> -C ₃ F ₇ • ^b
<i>k</i> _H	1.9 (±0.4) × 10 ⁵	4.9 (±0.8) × 10 ⁵	7.1 (±1.0) × 10 ⁶
<i>k</i> _H / <i>k</i> _D	3.45 ± 0.10	3.31 ± 0.14	2.9 ± 0.2
<i>k</i> _D	5.5 (±1.3) × 10 ⁴	1.49 (±0.30) × 10 ⁵	2.4 (±0.4) × 10 ⁶

^a Reference 17. ^b This work.

(3) Regioselectivity of H-Abstractions. For those substrates that had more than one position of likely reactivity, a measure of the regiochemistry of hydrogen abstraction was obtained by determining, for such substrates, both the position of deuterium incorporation and the extent of such incorporation by ²H NMR. The values given in Table 3 must be considered of undemonstrated accuracy with respect to the amount of actual H-abstraction at each site, because one could not be certain that the efficiency of trapping the regioisomeric radical intermediates was the same. However, a control reaction, the reduction of bromomethyl methyl ether, under identical conditions, led to a yield of 82% of dimethyl ether-*d*. Since the intermediate methoxymethyl radical, being nucleophilic and significantly stabilized, should be less reactive than an alkyl radical toward the silane reducing agent, we feel confident that most of the numbers in Table 3 are a reasonably accurate measure of the regioselectivity of H-abstraction. Another indication of the reliability of the numbers is a comparison of the rate constants for 1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane. The rate constants for abstraction of the C₄-H's from these two substrates are quite self-consistent, considering the deleterious steric impact of the latter's methyl substituents.

(4) Comparison of Fluorinated and Hydrocarbon Radicals. There are limited comparative data available from the literature regarding rate constants for analogous H-abstractions by *n*-alkyl radicals. Newcomb has reported rate constants for the reactions of the *n*-octyl radical with both THF and diethyl ether at 22 °C (4.9 × 10² and 1.15 × 10² M⁻¹ s⁻¹, respectively).^{21,22} Comparing these numbers with those given in Table 2 indicates that the *n*-C₄F₉• radical is 63 times more reactive toward THF and 191 times more reactive toward diethyl ether than is the *n*-octyl radical. Recently, a rate constant for the reaction of the primary, 2-methyl-2-phenylpropyl radical with dodecane at 100 °C was reported (3.5 × 10³ M⁻¹ s⁻¹).²³ When temperature-corrected using the "standard" value of log *A* = 8.5 for the preexponential factor recommended for H-abstrac-

tions,²⁴ and normalized for the number of hydrogens, it provides relative rates of 76 and 78 (*n*-C₄F₉• vs 2-methyl-2-phenylpropyl radical), using our Table 2 *k*_H values for *n*-heptane and cyclohexane, respectively.

Therefore, in those cases where rate constants are able to be compared, perfluoro-*n*-alkyl radicals are observed to be considerably more reactive than *n*-alkyl radicals with respect to C–H abstraction from organic substrates.

(5) Relative Reactivity of the Three Fluorinated Radicals.

Comparing the relative reactivities of the three fluorinated radicals, the summary data in Table 4 indicate that, for the three common substrates studied, the secondary perfluoroalkyl radical is *much* more reactive than the primary perfluoroalkyl radical, which itself exhibits little difference in reactivity from that of the primary tetrafluoroalkyl radical.

Since the bond dissociation energies for each of the types of C–H bonds being formed are not significantly different, one cannot attribute the observed differences in reactivity to enthalpic effects. The fact that the broadest range of reactivities is observed for H-transfer from the silane supports transition state polar effects being at least partially responsible for the differences in reactivity exhibited by the series of radicals, since silicon is a more electropositive atom than carbon.

Although the *i*-C₃F₇• radical is by far the most reactive, it also exhibits the greatest *selectivity* in its reactions, reacting with THF 20 times faster, per hydrogen, than cyclohexane, whereas *n*-C₄F₉• only has a ratio of 9 for its two respective rate constants. Not being pyramidal, the electrophilicity of *i*-C₃F₇• should be the main reason for its reactivity differences. Being more electrophilic than *n*-C₄F₉,²⁶ the greater reactivity of *i*-C₃F₇• again indicates the importance of polar effects in the transition state for C–H abstraction. Its particularly low rate constant for reaction with 1,4-dioxane probably reflects the greater electrostatic/field effects that should be exhibited by *i*-C₃F₇• than by *n*-C₄F₉•, although our rate data for this radical are too limited for a definitive conclusion about this at this time.

The Kinetic Impact of Substituents on C–H Abstraction by *n*-C₄F₉• Radicals. (1) Alkanes.

The reactivity of alkanes such as cyclohexane, cyclopentane, and *n*-heptane are very much what would be expected on the basis of the relative impact of thermodynamic, steric, and torsional influences on these substrates. On the basis of a recent quantitative study by Minisci of the regiochemistry of iodination of *n*-heptane by means of a free radical chain process that involved abstraction of hydrogen by *n*-C₄F₉•,²⁷ one can assign, using our experimental molar rate constant in Table 2 for the reaction of *n*-C₄F₉• with *n*-heptane, the absolute partial rate constants (per H) for reaction at each position on *n*-heptane. These rate constants are given in Table 5. The C₂ hydrogens of *n*-heptane are seen to be ~19 times

(20) For example, for cyclohexane and cyclopentane, the *molecular* rate constants have been divided by 12 and 10, respectively, to obtain the "per H" value in the last column of Table 2.

(21) Newcomb reported "pseudo-first-order" rate constants.²² These were converted to the given second-order rate constants by dividing his rate constants by the molarities of neat THF and diethyl ether (12.3 and 9.6 molar, respectively).

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Table 2. Kinetic Data for C–H Abstraction from Organic Substrates versus Si–D Transfer from *t*-BuMe₂SiD for Fluorinated Radicals^{a–c}

substrate	slope ^b	intercept	k_{H} overall/ $10^2 \text{ M}^{-1} \text{ s}^{-1 \text{ c}}$	k_{H} per H/ $10^2 \text{ M}^{-1} \text{ s}^{-1 \text{ c}}$	rel k_{H}
For <i>n</i> -C ₄ H ₉ C ₂ F ₄ ^{•c}					
1,4-dioxane	0.072 (±0.002)	0.07 (±0.02)	40 (±10)	10 (±2.5) ^h	1.5
cyclo-C ₆ H ₁₂	0.149 (±0.004)	0.086 (±0.04)	82 (±18)	6.8 (±1.4) ^d	1
THF	0.518 (±0.018)	0.10 (±0.04)	290 (±70)	67 (±18) ^{g,e}	10
For <i>n</i> -C ₄ F ₉ ^{•c}					
ClCH ₂ CH ₂ Cl	4.1 (±0.8) × 10 ⁻⁴	0.029 (±0.002)	0.6 (±0.25)	0.15 (±0.06) ^d	0.02
CH ₃ OH	0.0062 (±0.0003)	0.050 (±0.003)	9.2 (±1.9)	3 (±0.6) ⁱ	0.4
1,3,5-trioxane	0.0065 (±0.0008)	0.021 (±0.002)	9.7 (±2.3)	3.2 (±0.8) ^h	0.4
MeOCH ₂ OMe	0.013 (±0.002)	0.019 (±0.005)	19 (±5)	CH ₂ : 4.8 (±1.4) ^g CH ₃ : 1.6 (±0.5) ^g	0.6 0.2
C ₆ H ₁₃ Cl	0.0143 (±0.0012)	0.033 (±0.006)	21 (±6)	see Table 6	
CH ₃ OCH ₃	0.019 (±0.003)	0.035 (±0.03)	28 (±7)	4.7 (±1.2) ^d	0.6
1,4-dioxane	0.021 (±0.002)	0.023 (±0.008)	31 (±7)	7.8 (±1.7) ^h	1
2,2-dimethyl-1,3-dioxolane	0.030 (±0.002)	0.06 (±0.01)	45 (±10)	11 (±2.4) ^e	1.4
(CH ₃ CHOH) ₂ ^f	0.034 (±0.003)	0.044 (±0.010)	50 (±11)	25 (±6) ^e	3.2
mesitylene	0.041 (±0.008)	0.03 (±0.06)	61 (±17)	6.8 (±2) ⁱ	0.9
(CH ₃ OCH ₂) ₂	0.045 (±0.002)	0.015 (±0.01)	67 (±14)	CH ₂ : 11 (±2.4) ^g CH ₃ : 3.8 (±0.8) ^g	1.4 0.5
THP	0.047 (±0.004)	0.093 (±0.01)	70 (±15)	C ₂ : 22 (±4) ^{g,h} C _{3,4} : 4.4 (±1) ^g	2.8 0.6
<i>n</i> -heptane	0.051 (±0.002)	0.012 (±0.008)	76 (±16)	see Table 5	
cumene	0.051 (±0.007)	0.11 (±0.04)	76 (±19)	76 (±19) ^e	9.7
cyclo-C ₆ H ₁₂	0.063 (±0.002)	0.039 (±0.012)	93 (±20)	7.8 (±1.6) ^d	1
cyclo-C ₅ H ₁₀	0.070 (±0.004)	0.013 (±0.024)	104 (±22)	10.4 (±2.2) ^d	1.3
1,3-dioxolane	0.093 (±0.004)	0.024 (±0.018)	140 (±29)	C ₂ : 41 (±9) ^g C ₄ : 15 (±3.5) ^g	5.3 1.9
<i>i</i> -PrOH	0.110 (±0.004)	0.03 (±0.04)	163 (±33)	163 (±33) ^{e,g}	21
diethyl ether	0.149 (±0.006)	0.036 (±0.016)	220 (±50)	55 (±12) ^{e,g}	7
THF	0.207 (±0.004)	0.005 (±0.01)	310 (±61)	C ₂ : 71 (±15) ^{g,e}	9
tetrahydrothiophene	0.239 (±0.010)	-0.003 (±0.034)	355 (±73)	89 (±18) ^e	11.4
For <i>i</i> -C ₃ F ₇ [•]					
1,4-dioxane	0.0037 (±0.0004)	0.042 (±0.006)	89 (±18)	22 (±5) ^h	0.3
cyclo-C ₆ H ₁₂	0.0191 (±0.0014)	-0.001 (±0.008)	460 (±88)	38 (±7) ^d	1
THF	0.132 (±0.008)	-0.03 (±0.02)	3100 (±600)	780 (±150) ^e	20.5

^a Reactions were initiated with di-*tert*-butylhyponitrite (TBHN) at 36 ± 2 °C. Rate constants were derived from the rate constants of D-abstraction from *tert*-butyldimethylsilane-*d* ($k_{\text{D}} = 2.4 (\pm 0.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for *i*-C₃F₇[•], $k_{\text{D}} = 1.49 (\pm 0.30) \times 10^5$ for C₄F₉[•], and $k_{\text{D}} = 5.5 (\pm 1.3) \times 10^4$ for RC₂F₄[•] at 25 ± 2 °C). ^b Slopes were temperature independent, ±10 °C (see ref 17). ^c Rate constants are all for 25 ± 2 °C; errors are all 2σ. ^d All hydrogens in the molecule were taken into account. ^e Only α-hydrogens of CH or CH₂ type were taken into account. ^f Reaction was done in 1,2-dichloroethane. ^g See Table 3 for regiochemical data. ^h Only axial H's were taken into account. ⁱ Only CH₃ hydrogens were considered.

Table 3. Measured Regioselectivity of Hydrogen Abstraction from Selected Substrates^a

substrate	regioselectivity (%)	
THF	2: 92%	3: 8%
THP	2: 62	3 and 4: 38
diethyl ether ^b	α: 100	
2-propanol ^b	α: 100	
1,3-dioxolane ^c	2: 58	4: 42
CH ₃ OCH ₂ OCH ₃	CH ₂ : 50	CH ₃ : 50
CH ₃ OCH ₂ CH ₂ OCH ₃	CH ₂ : 66	CH ₃ : 34

^a Reactions were carried out in BTB, with *n*-C₄F₉I as abstracting species and PhMe₂SiD as deuterium transfer agent, using an excess of substrate. They were initiated by UV unless otherwise indicated. ^b *tert*-Butylhyponitrite was used for initiation at 40–45 °C. ^c The average value for three experiments.

more reactive than its methyl hydrogens, a result quite consistent with the ~3 kcal greater stabilization of a secondary versus a primary alkyl radical.²⁸ Slight differences in steric effects probably adequately explain the differences in C–H abstraction rates for cyclohexane ($k_{\text{H}}/10^2 \text{ M}^{-1} \text{ s}^{-1} = 7.8$ per H) and the various secondary H's of *n*-heptane. The secondary:primary selectivity exhibited by the *n*-C₄F₉[•] radical is somewhat greater than that reported by Walling for the *t*-BuO[•] radical (12:1).^{13a}

The slightly greater reactivity of the hydrogens of cyclopentane compared to those of cyclohexane ($k_{\text{rel}} = 1.3$ per H) can

(28) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765.

Table 4. Comparison of Molecular Rate Constants of Hydrogen Abstraction by *n*-C₄H₉CF₂CF₂[•], *n*-C₄F₉[•], and *i*-C₃F₇[•] for Specific Common Substrates

substrate	k_{rel}			
	RCH ₂ CH ₂ [•]	RCF ₂ CF ₂ [•]	<i>n</i> -C ₄ F ₉ [•]	<i>i</i> -C ₃ F ₇ [•]
cyclohexane	0.014 ^a	(1)	1.1	5.6
THF	0.017 ^b	(1)	1.1	11
1,4-dioxane		(1)	0.8	2.2
<i>t</i> -BuMe ₂ SiH	0.004	(1)	2.6	37
C–H BDE ^c	101.1	101–102 ^d	103.3	103.6

^a Reference 23. ^b Reference 22. ^c Reference 1. ^d Calculated value.²⁵

be rationalized as deriving from the relief of torsional strain during the H-abstraction from cyclopentane.^{8a} Similarly, the C-2 hydrogens of THF are more reactive than those (axial) of THP ($k_{\text{rel}} = 3.2$ per H).

(2) **Chloroalkanes.** Although an α-chloro substituent is thermodynamically radical-stabilizing,^{29,30} formation of such radicals by C–H abstraction, or abstraction of a hydrogen in the vicinity of a chloro substituent by the *n*-C₄F₉[•] radical, is observed to be significantly inhibited. Thus the overall per hydrogen reactivity of 1-chlorohexane is considerably less than

(29) (a) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062–3072. (b) Korth, H.-G.; Sicking, W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 715–719.

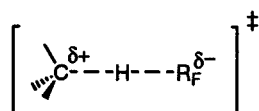
(30) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

Table 5. Derived Rate Constants for Hydrogen Abstraction from Each Position of *n*-Heptane by *n*-C₄F₉•

	position			
	1-CH ₃	2-CH ₂	3-CH ₂	4-CH ₂
% iodination ^a	4.1	51.0	30.3	14.6
total $k_{\text{H}}/10^2 \text{ M}^{-1} \text{ s}^{-1}$	3.1	38.8	23.0	11.1
$k_{\text{H}}/10^2 \text{ M}^{-1} \text{ s}^{-1}$ per H	0.52	9.7	5.8	5.6

^a Reference 26.**Table 6.** Derived Rate Constants for Hydrogen Abstraction from Each Position of 1-Chlorohexane by *n*-C₄F₉•

	position					
	1-CH ₂ Cl	2-CH ₂	3-CH ₂	4-CH ₂	5-CH ₂	6-CH ₃
% iodination ^a	2.1	3.5	12.0	26.7	50.0	5.7
total $k_{\text{H}}/10^2 \text{ M}^{-1} \text{ s}^{-1}$	0.44	0.74	2.5	5.6	10.5	1.2
$k_{\text{H}}/10^2 \text{ M}^{-1} \text{ s}^{-1}$ per H	0.22	0.37	1.3	2.8	5.3	0.4

^a Reference 26.**Figure 1.** Polar influences in H-abstraction transition state.

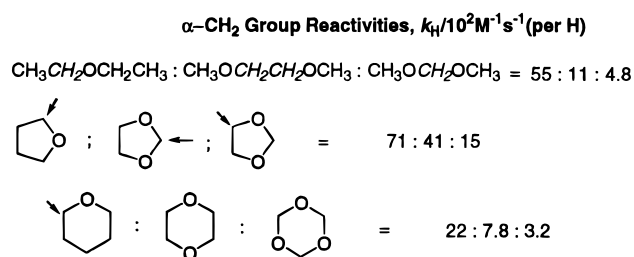
that of *n*-heptane ($k_{\text{rel}} = 3$). Using Minisci's regiochemical data for C–H abstraction from 1-chlorohexane (Table 6) to obtain rate constants for C–H abstraction from each of its individual carbons,²⁷ one can see that the (per H) rate constant for C–H abstraction from a methyl group of *n*-heptane is 2.4 times larger than that for the CH₂Cl carbon of 1-chlorohexane. Moreover, none of the CH₂ or CH₃ groups of 1-chlorohexane is as reactive as the analogous site in *n*-heptane!

Because the transition state, through bond, “polar” impact of the chlorine substituent should not be expected to extend more than two or three C–C bonds from C-1, this result was the first indication that *field effects* were intervening in these reactions.

The hydrogens of 1,2-dichloroethane are even less reactive ($k_{\text{rel}} = 0.67$) than those of the chloromethyl group of 1-chlorohexane.

The issue of the influence of electrostatic (field effects) on the rate constants of C–H abstractions by perfluoroalkyl radicals is worthy of particular emphasis at this point. Transition state “polar effects” are generally represented as being *inductive* in nature, and as such, they are not readily distinguished from electrostatic (field) effects, which generally predict the same trends in reactivities. For example, the chlorine substituents in 1,2-dichloroethane and 1-chlorohexane should not only inductively destabilize their H-abstraction transition states as shown in Figure 1, but they should also give rise to destabilizing electrostatic field interactions with the fluorine substituents of the perfluoroalkyl radicals within their abstraction transition states. Previously alluded to as “dipole–dipole interactions”,³¹ in recent years, Paleta has recognized the importance of such effects in alkene additions, referring to the detrimental electrostatic “tail effect” of perfluoroalkyl radicals as affecting the rates and regiochemistry of their additions to haloalkenes.³²

Insight into the importance of such field effects can be derived from a comparison of the data in Table 6 with related reactivity data of the *t*-BuO• radical.^{13c} It is noteworthy that, in its reaction

Scheme 3

with 1-chlorobutane, the *t*-BuO• radical, consistent with BDE considerations and despite its detrimental transition state polar influence, exhibited slightly greater reactivity with the C-1 than the C-2 hydrogens ($k_{\text{rel}} = 1.1$), in contrast to the analogous ratio of 0.6 that we observed for the *n*-C₄F₉• radical. We consider the difference in site selectivity for these two electronegative radicals to be largely the result of the significantly greater field effect of the *n*-C₄F₉• radical (vide infra).

(3) Ethers and Alcohols. As has been recognized by synthetic chemists for some time,³³ simple ethers, such as diethyl ether, THF, and THP, are among the most reactive substrates toward C–H abstraction by *n*-R_F•, with the α-CH₂ hydrogens of ether and THF having reactivities (per H) of 7 and 9, relative to those of cyclohexane. Likewise, the C–H bonds of methanol and dimethyl ether are 6 and 9 times more reactive, respectively, than those of *n*-heptane's methyl groups. Although such rate factors are generally consistent with thermodynamic expectations (i.e., the smaller BDE's of such bonds), this cannot be the entire story, since tetrahydrothiophene is even more reactive than THF, despite the probable higher BDE's of its α-hydrogens.²⁹ Such a result can best be rationalized in terms of the expected lower field effect for H-abstraction from tetrahydrothiophene.

(4) Molecules with More Than One Oxygen. Although a single ether function clearly activates its α-hydrogens with respect to abstraction, two or more ether functions in the same molecule, as exemplified in Scheme 3, give rise to a decrease in reactivity, sometimes substantial.³⁴ Although BDE differences (vide infra) are undoubtedly part of the reason for such reactivity differences, there is little doubt that polar, and especially field effects, also play an important role.

(5) C–H Bond Dissociation Energies: DFT Calculations. Because there are few experimental bond dissociation energies of ethers or alcohols available from the literature, and because we have previously found DFT to be quite satisfactory for calculating such values,²⁵ BDE's were calculated for some key model systems related to those ether and alcohol substrates examined in the current study. The computed BDE's in Table 7 are qualitatively consistent with both the regioselectivities of H-abstraction observed and the general trends in reactivity observed among mono-oxygen-substituted substrates in Table 2. However, as it will be seen, this BDE data cannot fully account for the observed lower reactivity of multi-oxygen-substituted substrates.

(6) Comparison of *n*-R_F• Reactivity Data with Those of the *tert*-Butoxyl Radical. The considerable rate data available for C–H abstraction processes of the electrophilic *t*-BuO• radical are relevant to our study of fluorinated radicals. Early data on *t*-BuO• were obtained by kinetic ESR experiments at temperatures between –30 and –60 °C,^{6–8} but more recently, laser

(33) (a) Chambers, R. D.; Kelly, N.; Musgrave, W. K. *J. Fluorine Chem.* **1980**, *16*, 351–364. (b) Chambers, R. D.; Grievson, B.; Kelly, N. *M. J. Chem. Soc., Perkin Trans. 1* **1985**, 2209–2214.

(34) The same is true for butane-2,3-diol, which is 3.3 times less reactive than 2-propanol.







(31) Gray, P.; Herod, A. A.; Jones, A. *Chem. Rev.* **1971**, *71*, 247–293.
(32) (a) Paleta, O.; Církva, V.; Budková, Z.; Böhn, S. *J. Fluorine Chem.* **1997**, *86*, 155–171. (b) Paleta, O.; Církva, V.; Kvícala, J. *J. Fluorine Chem.* **1996**, *80*, 125–134.

Table 7. DFT Computed Values for C–H Bond Dissociation Energies of Selected Ethers, Alcohols, and Esters (kcal/mol)

compd (C–H bond)	BDE, calcd (exptl)	compd (C–H bond)	BDE, calcd (exptl)
THF (2)	89.8 (92 ± 1) ^a	(CH ₃ O) ₂ CH–H	93.0
THF (3)	94.2	CH ₃ OCH ₂ OCH ₂ –H	94.3
1,3-dioxolane (2)	90.0	CH ₃ OCH ₂ –H	93.4 (93 ± 1) ^a
1,3-dioxolane (4)	91.5	CH ₃ OCH(CH ₃)-H	89.7
THP (2)	92.1	HOCH ₂ –H	93.6 (94.5 ± 0.2) ^a
1,4-dioxane	93.2	HOCH(CH ₃)H	91.0 (93 ± 1) ^a
1,3,5-trioxane	92.6	CH ₃ CH ₂ O ₂ CCH ₂ –H	95.4
		CH ₃ CO ₂ CH(CH ₃)-H	93.8

^a Experimental values derive from refs 27 and 29.

Table 8. Comparison of Molecular Rate Constants ($k/10^4 \text{ M}^{-1} \text{ s}^{-1}$)^a for C–H Abstraction by *t*-BuO• (300 K) versus *n*-C₄F₉• Radicals (298 K)

	$k_t/10^4 \text{ M}^{-1} \text{ s}^{-1}$		k_{rel} (<i>t</i> -BuO vs <i>n</i> -C ₄ F ₉)	BDE(kcal/mol) ^c	$k_{\text{rel}}(vs \text{ C}_6\text{H}_{12})$	
	<i>n</i> -C ₄ F ₉ • ^a	<i>t</i> -BuO• ^b			<i>n</i> -C ₄ F ₉ •	<i>t</i> -BuO•
	3.1	825	266	89.8	3.3	58
	1.4	770	550	90.0	1.5	54
	0.70	270	386	92.1	0.75	19
	0.097	195	2010	92.6	0.10	14
	0.31	150	484	93.2	0.33	10
	0.93	14.3	15.3	95.5 ^d	(1)	(1)

^a From column four of Table 2. ^b From ref 9c. ^c Weakest bond, from Table 7. ^d Reference 29.

flash photolysis experiments have allowed a broader range of substrates to be examined at room temperature.^{9,10} Table 8 presents a comparison of rate data for *t*-BuO• and *n*-C₄F₉• radicals.

From the data in Table 8, it can be seen that the *t*-BuO• radical is much more reactive than a *n*-R_f• radical toward C–H abstraction. This is in contrast to their more similar relative rates of hydrogen abstraction from stannanes, germanes, and silanes, where the $k_{t\text{-BuO}}/k_{n\text{-R}_f}$ values for *n*-Bu₃SnH, *n*-Bu₃GeH, and Et₃SiH are only 1.0, 6.6, and 7.6, respectively.

With the BDE's of *n*-R_f-H and *t*-BuO-H being similar (103 and 105 kcal/mol, respectively),^{25,30} any thermodynamic influence on the relative reactivities of the *t*-BuO• and *n*-C₄F₉• radicals should be minimal. Although both radicals should be highly electronegative, it is difficult to unambiguously assess their relative polar natures. (Whereas a consensus of calculations for CH₃O and CF₃ would give the former a greater group electronegativity,³⁵ the σ_m and F substituent constants³⁶ for CH₃O (0.12 and 0.29) and CF₃CF₂CF₂ (0.44 and 0.42) clearly indicate a stronger inductive electron withdrawing impact for the CF₃CF₂CF₂ group.) Therefore, at this time, suffice it to say that both radicals are highly electronegative and should exhibit significant transition state polar effects of the type depicted in Figure 1.

However, it appears that the *steric* and *field* effects of the two radicals are very different, with the *n*-R_f• radical exhibiting greater steric and field influences than the *t*-BuO• radical. Thus, in a process where polar effects should be significant and steric and field influences small, such as in H-abstraction from *n*-Bu₃SnH, the observed rates for *t*-BuO• and *n*-R_f• are similar. On the other hand, in reactions involving radical abstraction of

H from the less electropositive carbon atom, polar influences should be considerably diminished and steric effects magnified in importance. For such reactions, one observes the *t*-BuO• radical being considerably more reactive than the *n*-R_f• radical.

It is also notable that the *number of oxygen atoms* in the substrate appears to correlate with the magnitude of the *t*-BuO•/*n*-R_f• rate ratio. Thus with the number of ether functions being 0, 1, 2, and 3, the average rate ratios (from Table 8) are 15, 326, 517, and 2010, respectively. After the significant impact of the first oxygen, additional ether oxygens on the substrate do not have much of an effect on the *t*-BuO• radical's reactivity. Therefore, the observed trend in the *t*-BuO•/*n*-R_f• rate ratio can be attributed to the significant and increasingly *negative* impact of ether substituents on the k_{H} values of *n*-R_f•. The likely cause of this trend is transition state electrostatic repulsion between the perfluoroalkyl group of the radical and the oxygen atoms in the substrate. Note that all rates of C–H abstraction by the *t*-BuO• radical, *including that for cyclohexane*, are consistent with the respective C–H BDE's. In contrast, this is *not* the case for abstractions by *n*-R_f•, where the rate for cyclohexane is out of line—too fast. This can be interpreted as evidence that the rate constants for C–H abstraction from ethers by *n*-R_f• are *smaller* than would be predicted on the basis of BDE's alone, the probable reason being detrimental field effects.

Conclusions

A new competition kinetic methodology, which has been designed to obtain absolute rate constants for relatively slow hydrogen transfer processes of fluoroalkyl radicals, has been applied to obtain rate constants for hydrogen transfer from a variety of alkane, haloalkane, alcohol, and ether substrates. All of the studied fluoroalkyl radicals exhibit an enhanced reactivity relative to their hydrocarbon counterparts, with the secondary, *i*-C₃F₇• radical being substantially more reactive toward C–H abstraction than the *n*-C₄F₉• radical, a result indicating the importance of transition state polar effects in such reactions. Thermochemical, steric, and stereoelectronic factors also certainly play a role, but the most important conclusion derived from this study was the unambiguous realization that electrostatic, field effects strongly influence the reactivity of perfluoroalkyl radicals with organic substrates that contain electronegative atoms.

Experimental Section

Competition of Hydrogen Abstraction from *tert*-Butyldimethylsilane¹⁷ versus Addition to 2,3,4,5,6-Pentafluorostyrene for *i*-C₃F₇• Radical. The reactions were initiated with UV-light in Pyrex tubes. Ratios of [*i*-C₃F₇H]/[*i*-C₃F₇CH₂CH₂C₆F₅] were determined by integration of the CF₃ resonances (at δ_{F} –77.4 (dd, $J = 11.6, 5.6$ Hz) and –78 (d, $J = 6$ Hz) ppm, respectively) in the ¹⁹F NMR. The rate of hydrogen abstraction ($k_{\text{H}} = 7.1 (\pm 0.5) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) was determined by knowledge of the rate of addition of *i*-C₃F₇• to 2,3,4,5,6-pentafluorostyrene ($k_{\text{add}} = 8.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).³⁶

(35) (a) Datta, D.; Singh, S. N. *J. Phys. Chem.* **1990**, *94*, 2187–2190. (b) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271–7275. (c) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652–1655.

(36) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

The data for this study can be found in Table 9 in the Supporting Information.

Competition of H versus D Abstraction from *tert*-Butyldimethylsilane and *tert*-Butyldimethylsilane-*d*¹⁷ for *i*-C₃F₇ Radical. The reactions were initiated with di-*tert*-butylhyponitrite³⁸ at 37 °C. The overall concentration of the silanes was kept constant, and only their relative concentration was changed over the set of six tubes. Ratios of *i*-C₃F₇H/*i*-C₃F₇D were determined by the ratio of integrals of CFH and CFD resonances in the ¹⁹F NMR at –215.0 and –215.6 ppm, respectively. The $k_D = 2.4 (\pm 0.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ was then calculated from knowledge of the rate of H-abstraction from *t*-BuMe₂SiH which was determined in the previous experiment.

The data for this study can be found in Table 10 in the Supporting Information.

General Procedure for Competition Experiment of Hydrogen Abstraction from C–H Source versus Deuterium Abstraction from *tert*-Butyldimethylsilane-*d* for Nonfluorobutyl Radical. Each of six NMR tubes provided with the capillary glass tube containing solution of CFC₃ in C₆D₆ as an external standard for measuring ¹⁹F NMR was flushed with nitrogen and sealed with rubber septa. 1-Iodononafluorobutane, *tert*-butyldimethylsilane-*d*, and a hydrogen containing source were inserted by syringe. Each tube was filled with 1,3-bis(trifluoromethyl)benzene to the constant volume. Di-*tert*-butylhyponitrite³⁸ was added last. Concentration of the reactants was determined according to the weight ($\pm 0.001 \text{ g}$). The volume of the silane was kept constant through the set of six tubes, while the concentration of the C–H source was different for every sample. Each tube was 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 reaction was initiated with di-*tert*-butylhyponitrite at 34–38 °C until sufficient consumption of starting material was monitored by ¹⁹F NMR (usually ~24 h). Product ratios for each reaction mixture were determined by integration of ¹⁹F NMR resonances at –138.7 (dm, $J = 54 \text{ Hz}$, CF₂H) and –139.4 (m, CF₂D) ppm. Total yields of products *n*-C₄F₉H and *n*-C₄F₉D were generally 80–95% and were determined by the integration of fluorinated products and starting materials versus the CFC₃ resonance before and after the reaction. Since loss of either of the two products is unlikely, even in cases where yields were lower, such ratios were still considered an accurate measure of the relative rates of H- versus D-abstraction.

The slopes obtained from plotting [CF₂H]/[CF₂D] versus [C–H source]/[silane] provided the k_H/k_D ratio. The known k_D value was then used to determine the values of k_H given in Table 2.

Kinetic data for these studies can be found in Tables 14–36 in the Supporting Information.

Procedure for *n*-C₄H₉CF₂CF₂• Radical. The general procedure was the same as that for the *n*-C₄F₉• radical. The ratios of *n*-C₄H₉CF₂CF₂H/*n*-C₄H₉CF₂CF₂D for hydrogen abstraction from substrates versus deuterium abstraction from *t*-BuMe₂SiD were determined by integration of the CF₂H $\delta_F - 137$ (d, $J = 54 \text{ Hz}$) and CF₂D $\delta_F - 137.7$ (t, $J = 8 \text{ Hz}$) resonances in the ¹⁹F NMR spectra of the 1,1,2,2-tetrafluorohexane product.

Kinetic data for these studies can be found in Tables 37–39 in the Supporting Information.

Procedure for the *i*-C₃F₇• Radical. The procedure is the same as that used for the *n*-C₄F₉• radical. The ratios of *i*-C₃F₇H/*i*-C₃F₇D obtained for hydrogen abstraction from substrates versus deuterium abstraction from *t*-BuMe₂SiD were determined by integration of the product CFH and CFD resonances at –215 and –215.6 ppm, respectively, in the ¹⁹F NMR spectra of the 1,1,1,2,3,3,3-heptafluoropropane products.

The kinetic data for these studies can be found in Tables 11–13 in the Supporting Information.

Regioselectivity of Hydrogen Abstraction by *n*-C₄F₉• from Different C–H Sources. In a typical experiment 1-iodononafluorobutane

(37) Avila, D. V.; Ingold, K. U.; Luszyk J.; Dolbier, W. R., Jr.; Pan, H. Q. *Tetrahedron* **1996**, *52*, 12351–12356

(100 μL), C–H source (400–500 μL), and dimethylphenylsilane-*d* (150 μL) were introduced by syringe into a nitrogen-flushed NMR quartz tube sealed with rubber septa and secured with Parafilm tape. The tube was frozen in liquid nitrogen and subjected to three freeze–pump–thaw cycles followed by pressurization with nitrogen. The tube was subjected to UV photolysis in a Rayonet reactor at room temperature overnight. The reaction mixture was distilled to give fraction with bp < 90 °C free of silane-*d*. It was dissolved in CCl₄ for ²H NMR analysis. The selectivity of hydrogen abstraction was determined by integration of the deuterium resonances corresponding to the different sites of deuterated product.

Reduction of Bromomethyl Methyl Ether. Bromomethyl methyl ether (0.12 g), dimethylphenylsilane-*d* (0.24 g), benzene-*d*₆ (0.4 g), and *tert*-butyl peroxide (0.03 g) were delivered in a nitrogen-flushed NMR Pyrex tube sealed with rubber septa and secured with Parafilm tape. The tube was frozen in liquid nitrogen and subjected to three freeze–pump–thaw cycles followed by pressurization with nitrogen. The tube under vacuum was sealed with a burner and heated to 115 °C in an oil bath overnight to give complete conversion of the starting ether. Dimethyl ether-*d*, ¹H NMR δ 3.09 (t, 2H, $J = 1.5 \text{ Hz}$, CH₂D), 3.11 (s, 3H, CH₃), was formed in 82% yield by ¹H NMR. In a similar reaction in a Pyrex tube using UV light and *tert*-butyl peroxide (6 mol %) at room temperature for 3 days, 17% conversion and 80% yield of dimethyl ether-*d* were observed.

Computational Methods

Density functional theory calculations were performed using the Gaussian98W program package.³⁹ All substances and the radicals formed by H atom abstraction were optimized at Becke-style 3-Parameter (B3LYP)⁴⁰ density functional theory (DFT) level of theory using the 6-31G(d) basis set. Vibration frequencies were calculated at the same level of theory; all thermal energies were correct by factor 0.9804. Single point energy calculations were performed at the B3LYP level of theory using the 6-311+G(3df,2p) basis set (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)).

Bond dissociation energy is defined as the enthalpy (ΔH°) of eq 2. The enthalpy is obtained by the thermal correction of electronic energy of this equation to 298.15 °C, 1 atm, and then further corrected by ΔPV which is RT in this case.



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Supporting Information Available: Tables of kinetic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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