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Reactivity of Perfluoro-*n*-alkyl Radicals with Reluctant Substrates. Rates of Addition to $R_FCH_2CH{=}CH_2$ and $R_FCH{=}CH_2$

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Abstract: Conditions for conducting competitive experiments involving slow reactions of perfluoroalkyl radicals have been defined. A revised value for the rate constant for hydrogen abstraction from Et_3SiH is reported [(5.0 ±0.4) x 10^5 $M^{-1}s^{-1}$], as are the rate constants for addition of the *n*-C_4F_9• radical to $CH_2{=}CHCH_2C_4F_9$ [1.15 ± 0.11) x 10^6 $M^{-1}s^{-1}$] and to $CH_2{=}CHC_4F_9$ [2.6 ± 0.2) x 10^5 $M^{-1}s^{-1}$] at 25 °C. © 1998 Elsevier Science Ltd. All rights reserved.

Having demonstrated the remarkable electrophilic reactivity of perfluoroalkyl radicals via comprehensive laser flash photolysis and competition-based kinetic studies of their alkene addition and hydrogen abstraction reactions,[1,2] we now are proceeding to extend such studies to substrates of lower reactivity.

In the earlier work, it was demonstrated, for example, that highly electrophilic perfluoro-*n*-alkyl radicals exhibit dramatically enhanced reactivity, relative to the analogous hydrocarbon radicals, in their additions to *nucleophilic* alkenes, such as 1-hexene [$k_{add}(R_f\bullet)/k_{add}(R_H\bullet) \approx 30{,}000$). It was also shown that there was a quite respectable correlation of k_{add} with the ionization potentials of the 13 terminal olefins studied.[1a]

It was therefore expected that the π-bonds of the relatively electron-poor olefins, $CH_2{=}CHCH_2C_4F_9$ and $CH_2{=}CHC_4F_9$, with electronegative perfluoroalkyl substituents β and α, respectively, to the terminal π-bond, should be significantly less reactive than 1-hexene in undergoing additions by the highly electrophilic *n*-R_F• radical.

Although preliminary competition experiments confirmed this expected trend, it quickly became apparent that our normal approach for carrying out competition studies would not allow good quantitative data to be obtained for these systems. These preliminary studies demonstrated that, when measuring rates of such slow reactions, one must be *very* concerned about undesirable competitive reactions which are too slow to be of significance when one is measuring rates of fast reactions, but which can undermine the results from studies of slow reactions.

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For example, in studies of fast reactions, it was our normal procedure to use C_6D_6 as the solvent, without significant resulting problems. In the current study, however, products of radical addition to benzene were observed when it was used as solvent, thus lowering the yields of products from the desired competition processes and complicating the ^{19}F NMR spectra of the product mixtures to an unacceptable level.[3]

Another complication can arise when hydrogen atoms are donated to $R_F\bullet$ from sources other than the added Et_3SiH.[5] When both of the competitive processes under study are relatively slow (~ $10^5 M^{-1}s^{-1}$), then one has to worry about either the solvent or the alkene substrate itself competitively providing H-atoms to $R_F\bullet$.[8] In practice, one can readily determine when problems of this nature are intervening, because, in such situations the intercepts of the plots of [reduction product]/[addition product] versus $[Et_3SiH]/[alkene]$ (which are used to obtain k_H/k_{add} ratios) will deviate significantly from their ideal value of zero.

In order to obtain reliable data, one must strive to control these side reactions and thus to eliminate the problems which cause the non-zero intercept. Problems deriving from the solvent can usually be controlled. Numerous solvents have been carefully evaluated, and three have emerged as being generally satisfactory, exhibiting little propensity to either give up H-atoms or undergo addition by $R_F\bullet$. They are trifluoromethylbenzene, 1,4-bis(trifluoromethyl)benzene, and 1,3-bis(trifluoromethyl)benzene.[10]

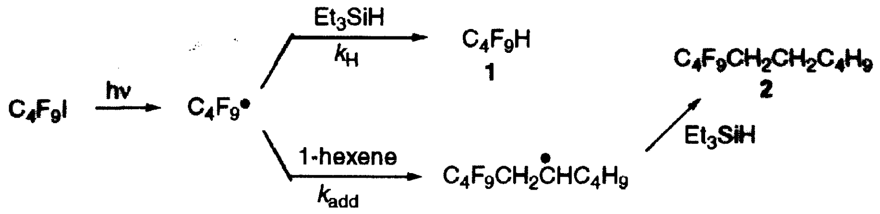
When the alkene addend is a possible source of H-atoms, then the problem can be addressed another way, by maintaining its concentration constant for each data point in the experiment (varying only the concentration of Et_3SiH), thus making the rate of such alternate H-atom donation constant, with the intercept becoming a *measure* of this rate, and the slope retaining its integrity as a true measure of $k_H(Et_3SiH)/k_{add}$(alkene addend).

Reassessment and redetermination of k_H for H-transfer from triethylsilane.

In the light of our present enhanced understanding of those factors which can contribute to inaccuracy in these competition studies,[12] we have gone back and reassessed *all* of our earlier experimental determinations of k_H values for H-transfer to n-$R_F\bullet$. So doing, we have found that all but one conformed reasonably to our criteria for an ideal competitive process, that being the measurement of the relatively small k_H for Et_3SiH. In spite of the good mass balance obtained in that study,[7] and in spite of the good correlation coefficient for the plot of the data, the intercept deviated significantly from zero, and, because we had not maintained [1-hexene] constant in this experiment, the previously reported rate constant must be considered suspect and of unreliable accuracy.

We have now reexamined this competition, using the competition depicted in Scheme 1 and modifying the conditions of the study so as to minimize any sources of error. 1,3-Bis-(trifluoromethyl)benzene was used as solvent, strict pseudo first order conditions were maintained for both Et_3SiH

Scheme 1. Competition System for Determination of k_H for Et_3SiH



and 1-hexene, and the concentration of 1-hexene was maintained constant for each point in the plot. As the data in Table 1 indicate, mass balances were good, the correlation coefficient was good, and the intercept was small, but significant. Ratios obtained from individual points were also not indicative of any significant problematic trend. Lastly, the ^{19}F NMR spectra of the crude product mixtures reflected formation of the reduction product **1**, and the addition product **2** as the only products containing fluorine. Thus, one can be confident that the obtained slope accurately reflects the ratio of k_H/k_{add}.

Table 1. Competition data for the photoinitiated reduction of perfluoro-*n*-butyl radical by triethylsilane versus its addition to 1-hexene in 1,3-bis(trifluoromethyl)benzene at 25 °C.

$[C_4F_9I]$	[1-hexene]	$[Et_3SiH/[1\text{-hexene}]$	[**1**]/[**2**]	Yield (%)
0.0431	0.463	4.330	0.283	96
0.0436	0.459	3.828	0.254	96
0.0441	0.468	3.319	0.220	94
0.0457	0.457	2.826	0.187	95
0.0431	0.468	2.234	0.155	94
0.0388	0.446	1.837	0.126	94

slope = 0.063 ± 0.001

intercept = 0.012

correlation coefficient = $r^2 = 0.999$

If one assumes that k_H' is the rate constant for H-atom abstraction from all sources other than the added reducing agent, Et_3SiH, then the expression which describes the ratio of reduction product, **1**, to addition product, **2**, is eq (1).

$$\frac{k_H[Et_3SiH]}{k_{add}[\text{alkene}]} + \frac{k_H'[\text{Other H-atom sources}]}{k_{add}[\text{alkene}]} = \frac{[1]}{[2]} \qquad \text{eq (1)}$$

In the special situation where the alkene addend is the only reasonable other H-atom source, the equation reduces to eq (2), where the slope will equal k_H/k_{add}, and the intercept will equal k_H'/k_{add}.

$$\frac{k_H[\mathrm{Et_3SiH}]}{k_{add}[\mathrm{alkene}]} + \frac{k_H'}{k_{add}} = \frac{[\mathbf{1}]}{[\mathbf{2}]} \qquad \text{eq (2)}$$

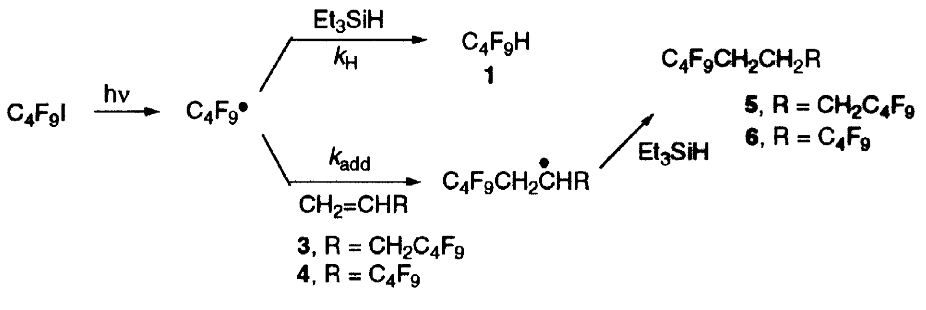
Taking the slope to be equal to k_H/k_{add}, and using the lfp-obtained value of k_{add} for the addition of n-$C_7F_{15}\bullet$ to 1-hexene ($7.9 \pm 0.7 \times 10^6\ M^{-1}s^{-1}$)[1a], one obtains a value of $5.0\ (\pm 0.4) \times 10^5\ M^{-1}s^{-1}$ as the rate constant (k_H) for abstraction of a hydrogen atom from Et_3SiH by a generic n-$R_F\bullet$ radical. This value differs slightly from the value of $7.5\ (\pm 0.7) \times 10^5\ M^{-1}s^{-1}$ which we had reported in 1995.[7]

Although one must be careful about giving the intercept too much quantitative significance, following through with the above logic leads to the conclusion that $k_H'/k_{add} = 0.012$, with the rate constant for H-atom abstraction from 1-hexene therefore being ca. $9 \times 10^4 M^{-1}s^{-1}$. Brace independently obtained a very similar value of 0.01 for the ratio of k_H'/k_{add} for 1-heptene in 1963,[13] so we can be reasonably confident about our interpretation of the data in this case.

Addition of n-$C_4F_9\bullet$ to $CH_2{=}CHCH_2C_4F_9$ and $CH_2{=}CHC_4F_9$.

The competitive studies of addition of perfluoro-n-butyl radical to the relatively unreactive alkenes, 4,4,5,5,6,6,7,7,7-nonafluoro-1-heptene (**3**) and 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (**4**), were carried out in trifluoromethylbenzene and 1,3-bis-(trifluoromethyl)benzene, respectively, using Et_3SiH as the hydrogen transfer agent as per Scheme 2. Because of the strengthening effect of a perfluoroalkyl group on neighboring

Scheme 2. Competition Studies to determine k_{add} values for alkenes **3** and **4**



$$\frac{k_H[\mathrm{Et_3SiH}]}{k_{add}[\mathbf{3}\ \text{or}\ \mathbf{4}]} = \frac{[\mathbf{1}]}{[\mathbf{5}\ \text{or}\ \mathbf{6}]} \qquad \text{eq (3)}$$

C-H bonds,[14] neither alkene was expected to donate hydrogen atoms at a rate competitive with Et_3SiH, and the small intercepts which were observed in the plots of data from Tables 2 and 3 using eq. (3) are consistent with this expectation.

Table 2. Competition data for the photoinitiated addition of perfluoro-*n*-butyl radical to 4,4,5,5,6,6,7,7,7-nonafluoroheptene (**3**) versus its reduction by triethylsilane in α,α,α-trifluoromethyl-benzene at 25 °C.

$[C_4F_9I]$	$[CH_2{=}CHCH_2C_4F_9]$	$[Et_3SiH]/[3]$	[1] / [5]	Yield (%)
0.043	0.541	2.44	1.11	92
0.043	0.619	1.98	0.894	84
0.043	0.699	1.624	0.728	99
0.043	0.752	1.423	0.668	98
0.045	0.654	1.591	0.754	106

Slope = 0.434 (±0.02)

Intercept = 0.04 (±0.04)

$r^2 = 0.992$

Table 3. Competition data for the photoinitiated addition of perfluoro-*n*-butyl radical to 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (**4**) versus reduction by triethylsilane in 1,3-bis(trifluoromethyl)benzene at 25 °C.

$[C_4F_9I]$	$[CH_2{=}CHC_4F_9]$	$[Et_3SiH]/[4]$	[1] / [6]	Yield (%)
0.051	1.558	0.385	0.80	100
0.052	1.566	0.479	0.902	96
0.047	1.569	0.570	1.118	99
0.050	1.565	0.699	1.302	95
0.051	1.567	0.820	1.58	95
0.049	1.570	1.012	2.00	91

Slope = 1.93 (±0.09)

Intercept = 0.01 (±0.06)

$r^2 = 0.992$

Comparative Reactivities of Fluorinated and Unfluorinated 1-Alkenes

	$k_{add}(M^{-1}s^{-1})$	k_{rel}
	7.9 (0.7) x 10^6	30
	1.15 (0.11) x 10^6	4.4
	2.6 (0.2) x 10^5	1

It can be seen that placing a perfluoroalkyl substituent proximate to a terminal π-bond has a significant detrimental effect with respect to its reactivity towards addition by a perfluoro-*n*-alkyl radical. This effect is no doubt largely the result of the large inductive electron-withdrawing effect of the perfluoroalkyl substituent on the inherent nucleophilicity of the hydrocarbon alkene. It has been demonstrated, by the correlation of k_{add} with alkene ionization potential in our earlier lfp study,[1a] that the major transition state orbital interaction for addition of the highly electrophilic perfluoroalkyl radical to alkenes is that between the SOMO of the radical and the HOMO of the alkene. Because of its great electronegativity, a proximate perfluoroalkyl substituent would certainly be expected to lower the energy of the alkene HOMO and thus make its π-bond less reactive towards addition by the R_F• radical.

When the C_4F_9 substituent is placed at the allylic position as in **3**, the rate constant for addition of the R_F• radical is ~ 7 times smaller than that for its respective addition to 1-hexene. Indeed, its rate constant is less than that for addition of R_F• to the acknowledged electrophilic olefin, acrylonitrile (k_{add} = 1.6 x 10^6 $M^{-1}s^{-1}$).[1a]

The rate constant for addition to **4**, where the C_4F_9 substituent is directly attached to the double bond, is the ***smallest*** rate constant for alkene addition that we have yet measured, either by lfp or by competition methods. Being able to obtain an accurate measure of this relatively small rate constant was an essential step in the process of extending our competition studies to increasingly slow reactions of perfluoroalkyl radicals. Indeed, within our current studies of inter- and intramolecular C-H abstraction processes we have now been able to reliably measure rate constants in the 10^3 range![9] These results will be reported in the near future.

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EXPERIMENTAL

General Procedure for the Kinetic Competition Experiments of Hydrogen Abstraction from Triethylsilane versus Addition to Olefins.

Into each of a set of pyrex NMR tubes flushed with nitrogen was added a known volume of the solvent. The quantities of silane, olefin, and perfluoro-*n*-butyl iodide in each sample were varied, with the respective amounts being weighed to determine their concentration. A thin, sealed glass tube containing a solution of (trifluoromethyl)trimethylsilane in C_6D_6 was placed in each tube as an external standard for measuring yields by ^{19}F NMR. Each NMR tube to be used for kinetics was frozen in *i*-PrOH/CO_2 mixture and subjected to three successive freeze-pump-thaw cycles followed by pressurization with nitrogen, and then finally sealed with a rubber septum and secured with parafilm tape. The tubes were then subjected to UV photolysis in a Rayonet reactor (254 nm) at room temperature until there was complete consumption of starting material, as monitored by ^{19}F NMR. The k_H/k_{add} ratios were determined from the plot of [Reduction Product]/[Addition Product] (as determined by ^{19}F NMR) versus [Et_3SiH]/[Olefin]. Yields were determined by integration of product resonances versus the external standard, (trifluoromethyl)trimethylsilane.

1,1,1,2,2,3,3,4,4,8,8,9,9,10,10,11,11,11-Octadecafluoroundecane (5). ^{1}H NMR δ ($CDCl_3$) 2.17 (tt, 4H, $C\underline{H_2}CF_2$, $^3J_{HF}$ = 18.5 Hz, $^3J_{HH}$ = 7.8 Hz), 1.96 (m, 2H); ^{19}F NMR (C_6D_6) δ -81.5 (t, 6F, J = 9.7 Hz), -115.2 (t, 4F, J = 13.3 Hz), -124.6 (t, 4F, J = 4.8 Hz), -126.3 (m, 4F); HRMS (CI) Calcd for $C_{11}H_5F_{17}$ ([M-HF]$^+$) 460.0120; Found: 460.0096; LRMS (EI) *m/z* 461 (1 %) [M-F]$^+$, 441 (3) [MH-2HF]$^+$, 421 (2) [MH-3HF]$^+$, 291 (44), 271 (20), 227 (100), 207 (21), 177 (14), 163 (18), 145 (11), 113 (13), 95 (19), 84 (16); 69 (17).

1,1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10,10-Octadecafluorodecane (6). ^{1}H NMR ($CDCl_3$) δ 2.40 (m, J = 12.4, 4.7 Hz); ^{19}F NMR ($CDCl_3$) δ -81.56 (t, 6F, J = 9.8 Hz), -115.45 (tm, 4F, J = 12.8 Hz), -124.8 (m, 4F), -126.54 (m, 4F); ^{13}C NMR ($CDCl_3$) δ 23.0 (tm, CH_2, J = 22.9 Hz) 106-124 (m, CF_2, CF_3 signals); HRMS (CI) Calcd for $C_{10}H_3F_{16}$ ([MH-2HF]$^+$) 426.9979; Found: 426.9970; LRMS (EI) *m/z* 445 (3), 427 (100) [MH-2HF]$^+$, 407 (79) [MH-3HF]$^+$, 357 (23), 277 (20), 257 (39), 213 (78), 195 (38), 163 (82), 145 (34), 113 (41), 95 (53), 69 (38).

The characterizations of all other products have been reported previously.[1a,7]

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