The reactivities of perfluoroisopropyl and *tert*-butyl radicals towards hydrogen atom abstraction from triethylsilane

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The rates of hydrogen abstraction from triethylsilane by the highly electrophilic perfluoroisopropyl and perfluoro-*tert*-butyl radicals have been obtained through competition experiments. These rates, 3.6×10^6 and 2.4×10^8 $\text{M}^{-1}\,\text{s}^{-1}$, respectively, are indicative of substantial reactivity enhancements, relative to perfluoro-*n*-alkyl radicals, derived from their enhanced electrophilicity and, in the latter case, from a much stronger forming C–H bond.

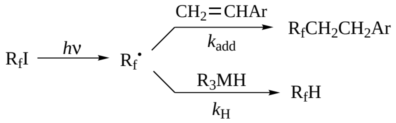
The unique reactivity characteristics of perfluoro-*n*-alkyl radicals with respect to alkene addition and hydrogen abstraction reactions have been attributed for the most part to two factors, their pyramidal nature and their great electrophilicity, with thermodynamics playing a relatively small role.[1,2] Furthermore, from studies of the reactivity of a series of partially fluorinated radicals, particularly those of the pyramidal but non-electrophilic radical $CH_3CH_2CH_2CH_2CF_2^{\bullet}$, in such processes, it was possible to conclude that pyramidality is less of a factor and thermodynamics more of a factor in hydrogen abstraction than in alkene additions processes.[3,4]

In a recent report on the alkene addition reactivity of the secondary and tertiary branched chain perfluoroalkyl radicals, $(CF_3)_2CF^{\bullet}$ and $(CF_3)_3C^{\bullet}$, we were able to conclude that such radicals are considerably more electrophilic than their primary counterparts.[5] Thus the rate constant for addition of the perfluoroisopropyl radical to styrene (1.2×10^8 M^{-1} s^{-1}) was a factor of 2.7 times larger, and that for the perfluoro-*tert*-butyl radical (3.7×10^8 M^{-1} s^{-1}) 8.6 times larger than that for the *n*-$C_3F_7^{\bullet}$ radical, such enhancements being remarkable in that: (*a*) there could be detrimental steric factors due to the larger size of these radicals, (*b*) the secondary and tertiary perfluoro radicals are not pyramidal and (*c*) the rates are within one order of magnitude of being diffusion controlled.

Recognizing the importance of charge transfer interactions in transition states for hydrogen atom transfer reactions, it was of interest to determine the reactivities of these highly electrophilic, but non-pyramidal secondary and tertiary perfluoroalkyl radicals in such a process. We now report that, just as the perfluoro-*tert*-butyl radical proved to be the most reactive carbon-based radical in its addition to electron-rich olefins such as styrene, it also turns out to be the most reactive yet studied in its ability to abstract a hydrogen atom from triethylsilane, more reactive even than the *tert*-butoxy radical.

Results

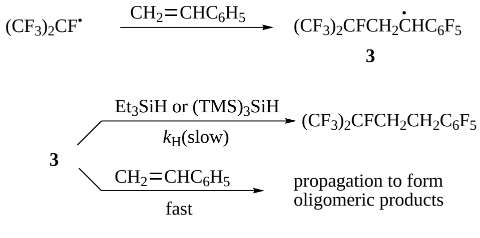
In order to obtain rate constants for hydrogen abstraction by the perfluoroisopropyl and *tert*-butyl radicals, it was necessary to generate these radicals under conditions where there would be an effective competition between the desired H-transfer and some alkene addition process for which the rates were known. For $(CF_3)_2CF^{\bullet}$, this necessity limited us to the use of either styrene or pentafluorostyrene for which we had values of k_{add}.[5] Within this practical limitation, we needed to find a combination of H-transfer agent and alkene which would lead to a clean competitive conversion to the reduction and the addition products, to the virtual exclusion of any other side products.



Initial experiments using Bu^n_3SnH and styrene indicated that the former would not be useful in the study. Bu^n_3SnH proved to be too effective a reducing agent to allow significant production of product deriving from addition to styrene. Moreover, in addition to the expected reduction process, $(CF_3)_2CFI$ apparently underwent an alternative reaction with Bu^n_3SnH, a process in which a coupled product was formed in about 90% yield, along with only 10% of the expected reduction product. Interestingly, neither $(CF_3)_3CI$ nor primary perfluoro-*n*-alkyl iodides exhibited such chemistry, both reacting with Bu^n_3SnH in the usual manner, giving largely the reduction product, R_fH.

$$Bu^n_3SnH + (CF_3)_2CFI \longrightarrow \underset{\sim 90\%}{Bu^n_3Sn\text{-}CF(CF_3)_2} + \underset{\sim 10\%}{HCF(CF_3)_2}$$

Styrene was completely ruled out as the possible alkene partner in the competition study when its oligomerization could not be effectively controlled. When using either $(TMS)_3SiH$ or Et_3SiH as the H-transfer agent, one always observed significant amounts of what appeared to be products deriving from further reaction of the propagating radical **3** with styrene. Apparently, use of the slower H-transfer agents did not allow for fast enough chain transfer to avoid oligomerization.



Fortunately, use of the combination of Et_3SiH/pentafluorostyrene alleviated all such problems. As seen in Tables 3 and 4, a satisfactory competition between reduction and addition coupled with an excellent mass balance, allowed us to meet the demanding criteria for satisfactory competition studies of both iso-$C_3F_7^{\bullet}$ and *tert*-$C_4F_9^{\bullet}$.

A plot of the data led, in each case, to a straight line (Figs. 1 and 2), the slope of which constituted the ratio of k_H/k_{add}. Since both values of k_{add} were known, these ratios could be converted into values for k_H, which are given in Table 1.

Table 1 Rate constants for hydrogen atom abstraction from triethylsilane by perfluoroisopropyl and *tert*-butyl radicals at 26 °C

Radical	k_H/k_{add}	$k_{add}/10^6$ M^{-1} s^{-1} $CH_2{=}CHC_6F_5$	k_{add}(rel)	$k_H/10^6$ M^{-1} s^{-1} [a]	k_H(rel)
$CF_3CF_2CF_2^\bullet$	—	13[b]	(1)	0.75[e]	(1)
$(CF_3)_2CF^\bullet$	0.44 ± 0.02	8.1[c]	0.62	3.6 ± 0.3	4.8
$(CF_3)_3C^\bullet$	14.7 ± 0.4	16[c]	1.2	240 ± 10	320
$RCH_2CH_2^\bullet$	—	0.31[d]	0.02	0.0007[f]	0.001

[a] Errors correspond to 2σ, and they are propagated. [b] Ref. 1. [c] Ref. 5. [d] Ref. 3. [e] Ref. 2. [f] Ref. 6.

Table 2 R_f–H bond dissociation energies

R_f–H bond	CH_3CH_2–H[a]	CF_3CF_2–H[a]	$CF_3CF_2CF_2$–H[b]	$(CF_3)_2CF$–H[b]	$(CF_3)_3C$–H[b]
BDE/kcal mol^{-1}	101.1	102.7	103.3	103.6	~109

[a] Ref. 14. [b] Ref. 15.

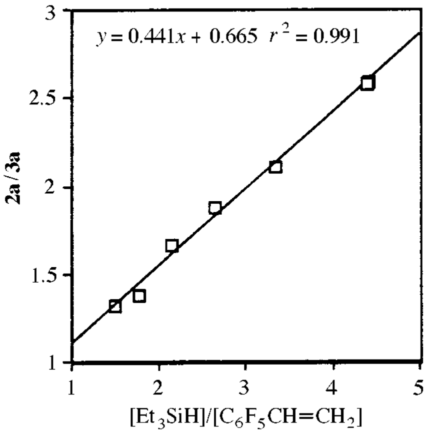
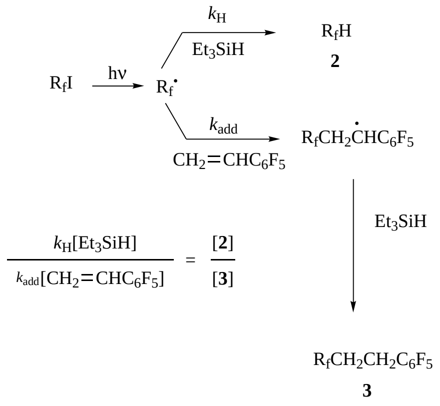


Fig. 1 Plot of the perfluoroisopropyl radical data from Table 3



Discussion

Traditionally, the reactivity of free radicals towards hydrogen atom abstraction is understood to be derived from a combination of bond-strength, steric and polarity effects.[7,8] When dealing with perfluoroalkyl radicals, we have shown that, when the radical bears at least two α-fluorine substituents, one must add to this list the factor of radical pyramidality.

In examining our kinetic data for the perfluoroisopropyl and perfluoro-*tert*-butyl radicals, it is obvious that the steric impact of these sterically-demanding secondary and tertiary radicals must be kinetically inconsequential. This, combined with the fact that neither of these radicals are pyramidal,[9–11] allows us to conclude that the nature of their reactivity can derive only from a combination of polar and bond-strength factors. This is consistent with the general recognition that free radical hydrogen atom abstractions are particularly sensitive to these two factors.[2,5,12,13]

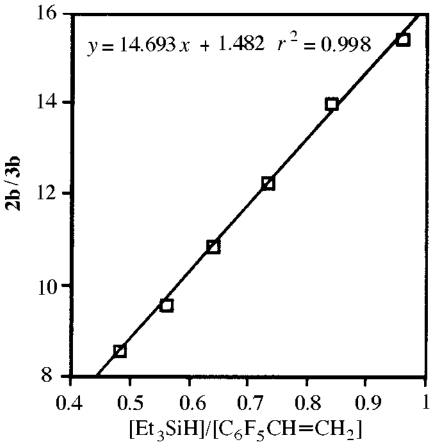


Fig. 2 Plot of the perfluoro-*tert*-butyl radical data from Table 4

What little pertinent experimental data exists related to C–H bond dissociation energies (BDEs) of perfluoroalkyl groups is listed in Table 2.†[14,15] To the extent that one trusts the reliability of this scant data, one must conclude that only in the perfluoro-*tert*-butyl case should bond-strength effects have a significant kinetic impact on relative radical reactivity with respect to hydrogen atom abstraction.

Regarding the importance of polar effects, on the basis of our study of the rates of alkene addition,[5] which included correlation of rate data with alkene ionization potentials, we concluded that both the perfluoroisopropyl and the perfluoro-*tert*-butyl radicals were highly electrophilic, with the latter being 'by far the most electrophilic carbon-centered radical' yet studied. σ_m values for n-C_3F_7, iso-C_3F_7 and *tert*-C_4F_9 (0.44, 0.47 and 0.55 respectively)[18] indicate strong electron attraction capacity for all three. Moreover, they imply that iso-$C_3F_7^\bullet$ should be more similar to n-$C_3F_7^\bullet$ than *tert*-$C_4F_9^\bullet$, with respect to polar influence. With little apparent incremental kinetic influence to be derived from C–H bond energy differences, the enhanced reactivity of iso-$C_3F_7^\bullet$, presumably largely derived from its enhanced electrophilicity, is more than sufficient to overcome its lack of pyramidality and make it *ca.* five times more reactive than iso-$C_3F_7^\bullet$ towards abstraction of a hydrogen atom from Et_3SiH.

The perfluoro-*tert*-butyl radical is much more reactive, being *ca.* 314 times more reactive than n-$C_3F_7^\bullet$ and 335 000 times more reactive than $RCH_2^\bullet$.[6] On the basis of the information available, we would conclude that its huge reactivity derives from a combination of the inordinately large BDE for the C–H

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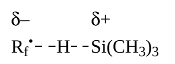
† Recent computational studies of C–H bond dissociation energies in HF calculations are consistent with the observed experimental trends.[4,16,17]



$$\overset{\delta-}{R_f^{\bullet}}\text{- -H- -}\overset{\delta+}{Si(CH_3)_3}$$

Fig. 3 Transition state for hydrogen atom abstraction

bond which is being formed†'‡ and the great electrophilicity of the radical, which allows the H-transfer process to benefit from a highly advantageous match-up of group polarizations in the reaction's transition state, as depicted in Fig. 3.

The large observed rate constant for hydrogen abstraction by *tert*-$C_4F_9^{\bullet}$ from Et_3SiH greatly exceeds even that for abstraction by the highly reactive, highly electrophilic *tert*-butoxy radical, $(CH_3)_3C\text{–}O^{\bullet}$ ($5.7 \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$),[19] thus making the perfluoro-*tert*-butyl radical the most avaricious hydrogen atom scavenger yet studied.

Experimental

Materials

Perfluoroisopropyl iodide and perfluoro-*tert*-butyl iodide were obtained from PCR and SynQuest, respectively. Both 2-H-perfluoropropane, **2a**, and 2-H-perfluoro-2-methylpropane, **2b**, have been synthesized and characterized previously.[20,21] All compounds used in this work were >96% pure, as determined by analytical GC ($\frac{1}{8}''$ × 10′ SE-30), and all products were purified by preparative GC using a $\frac{1}{4}''$ × 10′ SE-30 column. *J* Values are given in Hz.

Procedure for determination of the rate constant for H-atom transfer (k_H) to the perfluoroisopropyl radical from triethylsilane

Reaction sample tubes were prepared by adding 3 μl of perfluoroisopropyl iodide to [$^2H_6$]benzene in a Pyrex NMR tube to which appropriate amounts of triethylsilane and 2,3,4,5,6-pentafluorostyrene (PFS) had been added. Six such samples, varied in the amounts of triethylsilane and PFS (as indicated in Table 3) were needed to carry out the rate determination. Samples were sealed in the NMR tubes using rubber septa, degassed (freeze–thaw) three times under argon, and then photolysed using a Rayonet reactor for 22 h. ^{19}F NMR spectroscopy was used to monitor the reaction at room temperature and to quantitatively analyse the reduction and addition products. $PhCF_3$ was used as the internal standard to calculate the NMR yield of the reactions. The ratios of reduction product $(CF_3)_2CFH$ **2a**[18] to addition product **3a** were obtained by measuring the integrals of the appropriate peaks in the ^{19}F NMR spectrum: for **2a**, $(CF_3)_2CFH$, δ −76.44; for **3a**, $(CF_3)_2CF(CH_2)_2C_6F_6$, δ −76.96. These ratios, when plotted *versus* the respective [Et_3SiH]/[PFS] ratios, gave a straight line, the slope of which constituted the ratio k_H/k_{add}.

Procedure for determination of the rate constant for H-atom transfer (k_H) to the perfluoro-*tert*-butyl radical from triethylsilane

Reaction samples were prepared by adding 3 μl of perfluoro-*tert*-butyl iodide solution (6.9 M in [$^2H_6$]benzene) to [$^2H_6$]benzene in a Pyrex NMR tube to which appropriate amounts of triethylsilane and PFS were charged. The procedure thereafter corresponded to that for the perfluoroisopropyl radical. The corresponding peaks in the ^{19}F NMR spectrum were: for **2b**,‡ $(CF_3)_3CH$, δ −64.24; for **3b**, $(CF_3)_3C(CH_2)_2C_6F_5$, δ −67.06.

Table 3 Competition data for the reaction of perfluoroisopropyl radical with 2,3,4,5,6-pentafluorostyrene and triethylsilane at 298 K[a]

[$C_6F_5CH{=}CH_2$]	[Et_3SiH]/[$C_6F_5CH{=}CH_2$]	**2a/3a**	yield/%
0.54	1.49	1.32	97
0.48	1.77	1.38	98
0.42	2.15	1.66	99
0.36	2.64	1.88	96
0.30	3.34	2.11	96
0.24	4.39	2.59	95

[a] Computed slope = k_H/k_{add} = 0.44 ± 0.02.

Table 4 Competition data for the reaction of perfluoro-*tert*-butyl iodide with 2,3,4,5,6-pentafluorostyrene and triethylsilane at 298 K[a]

[$C_6F_5CH{=}CH_2$]	[Et_3SiH]/[$C_6F_5CH{=}CH_2$]	**2b/3b**	yield/%
1.09	0.48	8.56	97
1.03	0.56	9.59	96
0.97	0.64	10.88	98
0.92	0.73	12.27	98
0.86	0.84	14.02	96
0.80	0.96	15.43	98

[a] Computed slope = k_H/k_{add} = 14.89 ± 0.36.

Isolation of addition products, 3

In each case the addition products, **3**, were isolated by preparative GC from reaction mixtures characterized.

1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-(2,3,4,5,6-pentafluorophenyl)butane. δ_H(300 MHz; C_6D_6; TMS) 2.43 (t, *J* 8, 2H), 1.84 (m, 2H); δ_F(282 MHz; C_6D_6; $CFCl_3$) −76.96 (d, *J* 5, 6F), −145.29 (d of d, *J* 22, 7, 2F), −156.91 (t, *J* 22, 1F), −162.83 (d of d, *J* 22, 7, 2F), −185.62 (m, 1F); *m*/*z* (HR) found, 364.0114; $C_{11}H_4F_{12}$ requires 364.0121.

1,1,1-Trifluoro-2,2-bis(trifluoromethyl)-4-(2,3,4,5,6-pentafluorophenyl)butane. δ_H(300 MHz; C_6D_6; TMS) 2.52 (t, *J* 8, 2H), 1.92 (t, *J* 8, 2H); δ_F(282 MHz; C_6D_6; $CFCl_3$) −67.06 (s, 9F), −145.27 (d of d, *J* 22, 7, 2F), −156.41 (t, *J* 22, 1F), −162.36 (d of d, *J* 22, 7, 2F); *m*/*z* (HR) found, 395.0109; $C_{12}H_4F_{13}$ ($M^+ - F$) requires 395.0105.

Procedure for the reaction of perfluoroisopropyl iodide with tributyltin hydride

Tributyltin hydride (1.45 g, 5 mmol) was added to perfluoroisopropyl iodide (5 mmol, 1.48 g) in 5 ml benzene at 0 °C, and the solution was photolysed for 20 min under N_2. Perfluoroisopropyltributyltin was separated by distillation: bp 90 °C (1.25 mmHg); δ_H(300 MHz; C_6D_6; TMS) 1.62 (m, 6H), 1.31 (m, 12H), 0.94 (t, *J* 7, 9H); δ_F(282 MHz; C_6D_6; $CFCl_3$) −70.70 (d, *J* 15, 6F), −208.95 (m, 1F); *m*/*z* (HR) found, 460.1025; $C_{15}H_{27}F_7Sn$ requires 460.1022.

Acknowledgements

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‡ The strength of this bond no doubt derives largely from huge electrostatic effects which are the result of the nine fluorine substituents which are β to the C–H bond.[4] According to preliminary calculations of atomic charges [B3LYP/6-31G(d)], points selected by the MKS fitting scheme), electrostatics contribute little to C–H BDEs in hydrocarbons (CH_3CH_2–H, −0.05 and +0.02), give rise to slight electrostatic repulsion in CF_3CF_2–H (+0.17 and +0.12), and give rise to modest electrostatic attraction for $(CF_3)_2CF$–H (−0.11 and +0.17) and significant electrostatic attraction for $(CF_3)_3C$–H (−0.36 and +0.23).[4,17]

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