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Absolute Rate Constants for Some Reactions of Perfluoro-*n*-alkyl Radicals in Solution[1]

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Abstract: Absolute rate constants have been measured at 298 ± 2 K for some reactions of $C_2F_5^•$, n-$C_3F_7^•$, n-$C_7F_{15}^•$, and n-$C_8F_{17}^•$ by time-resolved (laser flash photolysis) and competition kinetics. The last three of these radicals exhibit essentially equal reactivities, but $C_2F_5^•$ is somewhat more reactive. The strongly electrophilic nature of these radicals is illustrated by an outstanding Hammett correlation for the addition of n-$C_8F_{17}^•$ to four para-substituted styrenes, $\log(k^X_{add}/k^H_{add}) = -0.53\sigma$, $\langle r \rangle = 0.99$ (X = p-CH_3O to p-CF_3), and, far more significantly, by a respectable correlation, $\langle r \rangle = 0.97$, of $\log k_{add}$ with the ionization potentials (IP) of 13 terminal olefins, the values of k_{add} for n-$C_3F_7^•$ ranging from 1.6×10^6 to 2.2×10^6 $M^{-1}\,s^{-1}$ for $CH_2{=}CHCN$ (IP = 10.91 eV) to 7.9×10^7 to 8.9×10^7 $M^{-1}\,s^{-1}$ for α-methylstyrene (IP = 8.19 eV). The n-$C_8F_{17}^•$ radical is 100 times as reactive in hydrogen atom abstraction from tri-n-butyltin hydride as an n-alkyl radical, with k^H_{abs} (n-$C_7F_{15}^•$) = 2.0×10^8 $M^{-1}\,s^{-1}$.

In recent years there has been considerable effort devoted to obtaining a fundamental understanding of those factors which govern the reactivities of radicals in their bimolecular reactions with organic substrates, particularly with regard to carbon–carbon bond formation, which generally involves the addition of carbon-centered radicals to alkenes. Reactivity in radical additions to alkenes is recognized to derive from a "complex interplay of polar, steric, and bond-strength terms",[4] which is very much influenced by the nature and position of substituents on both the radical and the alkene.[3–7] Insights which have resulted from past work in this field include the conclusions that (1) substituents at the carbon atom of the alkene which is not attacked (β-substituents) exert predominantly polar effects on the rates of addition; (2) substituents at the carbon atom which is attacked (α-substituents) exert both polar and steric effects; and (3) substituents at the radical center exert both polar and steric effects on the rate of addition to alkenes.

Additions of carbon-centered radicals to alkenes are generally strongly exothermic, since a σ-bond is formed at the expense of a π-bond (e.g., addition of methyl radical to styrene has a $\Delta H° = -38.5$ kcal/mol). Thus, according to the Hammond postulate,[8] such reactions should have early transition states with little bond-making or bond-breaking. This is supported by the fact that measured activation energies for such additions generally lie between 3 and 8 kcal/mol[9] and by theoretical calculations which indicate unsymmetrical transition states which are relatively independent of the electrophilic or nucleophilic nature of the radical species and which indicate an approach to bonding to the α-carbon in which the radical is far removed from the β-carbon.[10–12]

An early transition state, the energy of which is dominated by polar effects, suggests that the reaction can best be described in terms of frontier molecular orbital theory.[13,14] Essentially this theory states that energy differences between the highest occupied molecular orbital (HOMO) of one reactant and the lowest unoccupied molecular orbital (LUMO) of the other reactant are decisive in determining variations in reaction rate: the smaller the difference in energy, the faster the predicted rate of reaction.[15,16] Since the highest occupied orbital of a free radical is the SOMO (singly occupied molecular orbital), the energy difference between the SOMO and the alkene HOMO and/or LUMO should be of considerable importance in determining the rates of radical additions to alkenes.

Direct, time-resolved methods have been extensively employed to obtain absolute kinetic data for a wide variety of alkyl radical reactions in the liquid phase,[17] and there are presently considerable data available for alkene addition reactions of highly nucleophilic radicals, such as the *tert*-butyl radical.[6,18] Such data indicate that the reactivity of (nucleophilic) alkyl radicals can be understood as deriving from a dominant SOMO–LUMO interaction. Accordingly, the rates of addition of alkyl radicals correlate very well with the electron affinities (EAs) of the substrate alkenes.

Very recently, data have begun to appear for addition reactions of "electrophilic" radicals. Thus, the reactivity patterns for the dicyanomethyl radical imply that the SOMO–HOMO interaction is important in the transition state because there is a rough correlation of addition rates with the ionization potentials (IPs)

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(3) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 753–764.

(4) Tedder, J. M.; Walton, J. C. *Acc. Chem. Res.* **1976,** *9,* 183–191. Tedder, J. M.; Walton, J. C. *Tetrahedron* **1980,** *36,* 701–707.

(5) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982,** *21,* 401–410.

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

(7) Stefani, A. P. *Fluorine Chem. Rev.* **1971,** *5,* 115–177.

(8) Hammond, G. S. *J. Am. Chem. Soc.* **1955,** *77,* 334–338.

(9) Abell, P. I. In *Comprehensive Chemical Kinetics;* Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol. 18, Chapter 3, pp 111–165.

(10) Hoyland, J. R. *Theor. Chim. Acta* **1971,** *22,* 229–233.

(11) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1978,** *100,* 5290–5295.

(12) Zipse, H.; He, J.; Houk, K. N.; Giese, B. *J. Am. Chem. Soc.* **1991,** *113,* 4324–4325.

(13) Salem, L. *J. Am. Chem. Soc.* **1968,** *90,* 543–552.

(14) Fukui, K. *Fortschr. Chem. Forsch.* **1970,** *15,* 1. Fukui, K. *Theory of Orientation and Stereoselection;* Springer-Verlag: Berlin, 1975.

(15) Houk, K. N. *Acc. Chem. Res.* **1975,** *8,* 361–369.

(16) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972,** *11,* 838–840.

(17) Landolt-Börnstein. In *New Series, Radical Reaction Rates in Liquids;* Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Parts a, b.

(18) Heberger, K.; Walbiner, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 635–636.

0002-7863/94/1516-0099$04.50/0

of the substrate alkenes.[19] The additions to alkenes of "ambiphilic" radicals, including perhaps the malonyl radical and certainly the (*tert*-butoxycarbonyl)methyl radical, have also been studied.[20-22] These radicals exhibit an intermediate behavior, giving U-shaped correlation plots of log k versus substrate EAs or IPs.

The above-mentioned electrophilic and ambiphilic radicals derive their electrophilicities from π-delocalization of the carbon-centered radical onto electron-attracting substituents. However, there have been virtually no alkene addition rate measurements for radicals which derive their electrophilicities largely from inductive effects. Specifically, in spite of the huge amount of qualitative literature on the radical chemistry of perfluorinated substrates, there have been until now virtually no measurements of absolute rate constants for alkene addition reactions of perfluoroalkyl radicals in solution.

Certainly one would expect the absolute reactivities of alkyl and perfluoroalkyl radicals to differ significantly, since the former are electron-rich, planar π-radicals, whereas the latter are electron-poor, nonplanar σ-radicals. Moreover, the addition reactions of perfluoroalkyl radicals should be considerably more exothermic than those of their hydrocarbon counterparts.[23] Because the effective use of fluoroalkyl radicals in organic synthesis, polymer chemistry, and so on requires a proper understanding of their reactivity *vis-à-vis* the reactivity of structurally related alkyl radicals, we have begun a program to measure the absolute kinetics of prototypical fluoroalkyl radical reactions using a combination of laser flash photolysis (LFP), product analyses, and conventional competitive kinetics.

Results

Laser Flash Photolysis Experiments. In the present study,[27] we have examined the alkene addition reactions of $C_2F_5^\bullet$, n-$C_3F_7^\bullet$, and n-$C_7F_{15}^\bullet$. Each of these radicals was generated "instantaneously" by photolysis of the parent diacyl peroxide **1**[28] (ca. 0.16 M in $CFCl_2CF_2Cl$ at room temperature) using 308-nm light pulses from an excimer laser (reaction 1). The perfluoroacyloxyl radicals produced initially decarboxylate rapidly to yield the perfluoroalkyl radicals.

$$\underset{\mathbf{1}}{(R_fC(O)O)_2} \xrightarrow[308\text{ nm}]{h\nu} 2R_fCO_2^\bullet \xrightarrow[-CO_2]{\text{fast}} 2R_f^\bullet \qquad (1)$$

$$R_f = C_2F_5,\ n\text{-}C_3F_7,\ n\text{-}C_7F_{15}$$

The additions of the perfluoroalkyl radicals to styrene, α-methylstyrene, and β-methylstyrene were monitored directly *via* observation of the pseudo-first-order growth of the absorption at ca. 320 nm, as shown in Figure 1, which resulted from the formation of the benzylic radicals **2** (reaction 2). The rate constants for the "global" reactions of $R_f^\bullet$ with the styrenes, k_{gl}, were calculated from the experimental growth curves measured over a range of substrate concentrations, eq I.

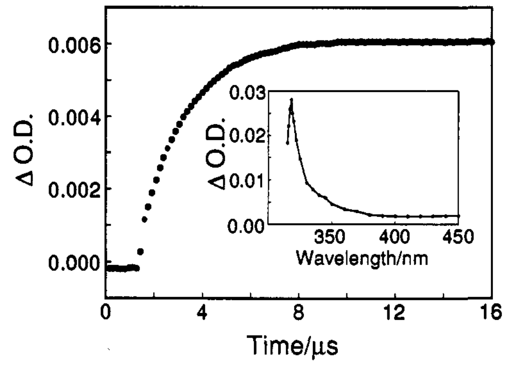

Figure 1. Growth of the 320-nm absorption assigned to the benzylic radical formed upon addition of $C_2F_5^\bullet$ to β-methylstyrene (0.038 M) in Freon 113. Inset shows the UV–visible spectrum of the product radical obtained 2 μs after LFP of a solution of $(C_2F_5C(O)O)_2$ in Freon 113 containing 0.38 M β-methylstyrene.

$$R_f^\bullet + RCH{=}CR'C_6H_5 \xrightarrow{k_{add}} \underset{\mathbf{2}}{R_fCH(R)\dot{C}R'C_6H_5} \qquad (2)$$

$$(\lambda_{max} \sim 320\text{ nm})$$

$$R,R' = H;\quad R = H,\ R' = CH_3;\quad R = CH_3,\ R' = H$$

$$k_{exptl} = k_0 + k_{gl}[RCH{=}CR'C_6H_5] \qquad (I)$$

Rate constants for the global reactions of $R_f^\bullet$ with a large number of other olefins and an acetylene which do not form easily observed products were also obtained by LFP at ambient temperature using 0.11 M β-methylstyrene as a spectroscopic "probe", eq II.[29]

$$k_{exptl}(320\text{ nm}) = k_0 + k_\beta[CH_3CH{=}CHC_6H_5] + k_{gl}[\text{substrate}] = k_0' + k_{gl}[\text{substrate}] \qquad (II)$$

To determine what fraction of k_{gl} for the two methylstyrenes should be assigned to addition (k_{add}) and what fraction assigned to possible H-atom abstraction reactions (k_{abs}), eq III,these two

$$k_{gl} = k_{add} + k_{abs} \qquad (III)$$

compounds were allowed to react with n-C_4F_9I in degassed cyclohexane at room temperature (RT) under radical chain conditions (initiation by UV irradiation, 10 h). The products were analyzed quantitatively by ^{19}F NMR using $C_6H_5CF_3$ as an internal standard. No n-C_4F_9H was formed, the only product in each case being that of 1:1 addition (reaction 3).

$$n\text{-}C_4F_9I + CHR{=}CR'C_6H_5 \xrightarrow[\text{cyclohexane, RT, 10h}]{h\nu} \text{only } n\text{-}C_4F_9CH(R)C(I)(R')C_6H_5 \quad \text{no } n\text{-}C_4F_9H \text{ observed} \qquad (3)$$

In a similar experiment with cyclohexene (AIBN initiated, 60 °C, 50 h), however, 7.2% of the H-atom abstraction product, n-C_4F_9H, was obtained.[30] Since all of the other substrates examined are terminal alkenes or alkynes, it would appear safe to assume that H-atom abstraction can be neglected except in the case of cyclohexene.[30] We therefore equate k_{gl} with k_{add} for all of the substrates studied except cyclohexene.

The rate constants, k_{add}, obtained from the LFP experiments for addition of the perfluoro-n-alkyl radicals to the various alkenes and an acetylene are given in Table I.

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[19] Riemenschneider, K.; Bartels, H. M.; Dornow, R.; Drechsel-Grau, E.; Eichel, W.; Luthe, H.; Matter, Y. M.; Michaelis, W.; Boldt, P. *J. Org. Chem.* **1987**, *52*, 205–212.

[20] Giese, B.; He, J.; Mehl, W. *Chem. Ber.* **1988**, *121*, 2063–2066.

[21] Santi, R.; Bergamini, F.; Citterio, A.; Sebastiano, R.; Nicolini, M. *J. Org. Chem.* **1992**, *57*, 4250–4255.

[22] Beranek, I.; Fischer, H. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Amsterdam, 1989; pp 303–316.

[23] Although there is a paucity of reliable data available, the CF_3–CH_3 bond dissociation energy (101 kcal/mol)[24] would appear to be about 11 kcal greater than that for CH_3–CH_3 (90 kcal/mol).[25,26]

[24] Rodgers, A. S.; Ford, W. G. F. *Int. J. Chem. Kinet.* **1973**, *5*, 965–975.

[25] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

[26] Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 3304–3306.

[27] Reported partially in preliminary form: Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Dolbier, W. R., Jr.; Pan, H.-Q. *J. Am. Chem. Soc.* **1993**, *115*, 1577–1579.

[28] Zhao, C.; Zhou, R.; Pan, H.; Jin, X.; Qu, Y.; Wu, C.; Jiang, X. *J. Org. Chem.* **1982**, *47*, 2009–2013.

[29] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

[30] Brace, N. O. *J. Org. Chem.* **1963**, *28*, 3093–3102.

Table I. Absolute Rate Constants for the Reactions of Perfluoro-*n*-alkyl Radicals with Various Unsaturated Substrates at 298 ± 2 K, as Measured by LFP (literature data on the absolute constants for some alkyl radical additions to olefins at the same temperature are given for comparison)

	$k_{add}/10^6$ M^{-1} s^{-1} [a]			$k_{add}/10^3$ M^{-1} s^{-1} [b]	
substrate [IP (eV)][c]	n-$C_3F_7^{\bullet}$	n-$C_7F_{15}^{\bullet}$	$C_2F_5^{\bullet}$	$RCH_2CH_2^{\bullet}$	$(CH_3)_3C^{\bullet}$
1. β-methylstyrene [8.10]	3.8 ± 0.2	3.7 ± 0.2	7.0 ± 0.8		
2. α-methylstyrene [8.19][d]	78 ± 8	89 ± 1	94 ± 16	59[e]	
3. styrene [8.43]	43 ± 1	46 ± 6		120[e]	132[f]
4. 4-$CF_3C_6H_4CH{=}CH_2$	29 ± 8	24 ± 3			
5. $C_6F_5CH{=}CH_2$ [9.20]	13 ± 1				
6. 1,4-dimethylenecyclohexane [9.12][g]	41 ± 3			0.13[h,i]	
7. 1-hexene [9.44]	6.2 ± 0.2	7.9 ± 0.7	16 ± 1	0.2[h,j]	
8. cyclohexene [8.94]	$1.3_0 \pm 0.0_5$[k]				
9. $HC{\equiv}CC(Me)_2OH$ [10.18][l]	$0.9_7 \pm 0.0_5$				
10. $H_2C{=}CHC(Me)_2OH$ [9.90]	2.8 ± 0.3				
11. $H_2C{=}CMeC(O)OMe$ [9.70]	19 ± 1				
12. $H_2C{=}CCl_2$ [9.79]	5.2 ± 0.3				350[f]
13. $H_2C{=}CHCN$ [10.91]	2.2 ± 0.1	1.6 ± 0.3	3.2 ± 0.3		2400[m]

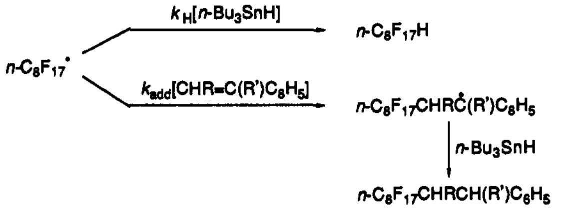
[a] This work, errors correspond to 2σ but include only random errors. [b] Literature data, note 1000-fold change in scaling factor. [c] For consistency we have taken all the IPs, unless otherwise noted, from the NIST Standard Reference Database 25. *NIST Structures Properties Database and Estimation Program 1991*; U.S. Department of Commerce: Gaithersburg, MD 20899, 1991. These values may differ slightly from those given in our original communication.[27] [d] The IP of α-methylstyrene does not reflect its HOMO energy in the transition state, because in the ground state the double bond is twisted out of the phenyl ring plane, see: Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans.* 2 **1973**, *69*, 196–206. [e] From Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2674–2682, as modified for temperature and other factors in Table III of ref 35. [f] From Münger, H.; Fischer, H. *Int. J. Chem. Kinet.* **1985**, *17*, 809–829. [g] IP taken as for methylenecyclohexane and log(0.5k_{add}) used in the plot of log k vs IP. [h] From ref 17 part a, p 160. [i] Reaction is $C_2H_5^{\bullet} + H_2C{=}C(CH_3)_2 \rightarrow C_3H_7C^{\bullet}(CH_3)_2$. [j] Addition of $C_2H_5^{\bullet}$. [k] Note k_{gl} value, $k_{add} = 1.21 \times 10^6$ M^{-1} s^{-1}. [l] IP taken from Levin, R. D.; Lias, S. G. *National Bureau of Standards: Ionization Potential and Appearance Potential Measurements, 1971–1981*. U.S. Government Printing Office: Washington, DC, 1982. [m] Taken from Jent, F.; Paul, P.; Roduner, E.; Heming, M.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 1113–1122.

Proof that we were indeed observing the addition reactions of the perfluoro-*n*-alkyl radicals and not those of some other reactive species (such as the perfluoroacyloxyl radical precursors) was provided by a determination of the rate constant for addition of $C_2F_5^{\bullet}$ radicals to β-methylstyrene using C_2F_5I as the source of the perfluoroethyl radical. The rate constant obtained by LFP of C_2F_5I, viz., $k_{add} = (6.1 \pm 1.3) \times 10^6$ M^{-1} s^{-1}, is equal within experimental error to the value obtained by LFP of the diacyl peroxide, viz., $k_{add} = (7.0 \pm 0.8) \times 10^6$ M^{-1} s^{-1}.

Competition Experiments

(a) Rate of H-Atom Abstraction from *n*-Bu$_3$SnH. Tri-*n*-butyltin hydride is one of the commonest organic reagents employed in organic syntheses which utilize radical chain reactions to obtain the desired product, including those syntheses in which a new C–C bond is formed in one step of the chain. For synthetic strategic planning, it is therefore extremely useful to know how rapidly different classes of carbon-centered radicals abstract hydrogen from the tin hydride, i.e., how rapidly are the carbon radicals involved in the synthesis going to be hydrogen-atom "capped" by the tin hydride. A direct attempt to measure the rate constant for the perfluoroalkyl radical/tin hydride reaction by LFP was frustrated by the occurrence of a direct and rapid thermal reaction between the tin hydride and the radical precursors (diacyl peroxides and iodides). We therefore resorted to a competitive method.

$$n\text{-}C_8F_{17}I \xrightarrow[C_6D_6]{h\nu,\ 1\ h} n\text{-}C_8F_{17}^{\bullet} \qquad (4)$$



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(5)

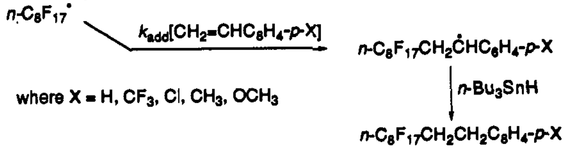
The competition involved attack of n-$C_8F_{17}^{\bullet}$ on n-Bu_3SnH relative to its addition to styrene or to α- or β-methylstyrene. The n-$C_8F_{17}^{\bullet}$ was generated (in a photoassisted reaction) from n-$C_8F_{17}I$ at room temperature. The relative concentrations of each pair of reagents were varied but were initially chosen so as to ensure comparable amounts of the two products, n-$C_8F_{17}H$ and the adducts **3**. The ratios of these products were determined, along with the absolute yields for the reactions, by ^{19}F NMR of the crude product mixtures, using (trifluoromethyl)benzene as the internal standard (reactions 4 and 5). The absolute yields of n-$C_8F_{17}H$ plus **3** in these and related (*vide infra*) experiments were in the range 93–98%. The rate constant ratio k_H/k_{add} was obtained by plotting $[n\text{-}C_8F_{17}H]/[3]$ vs $[n\text{-}Bu_3SnH]/[\text{styrene}]$ according to the kinetic relationship of eq IV.

$$\frac{[n\text{-}C_8F_{17}H]}{[3]} = \frac{k_H}{k_{add}} \cdot \frac{[n\text{-}Bu_3SnH]}{[\text{styrene}]} \qquad \text{(IV)}$$

Since the absolute rate constants, k_{add}, for addition of n-perfluoroalkyl radicals to these same styrenes had already been determined, we could calculate a value for k_H from each of these n-Bu_3SnH–styrene competitions. As one can see from Table II, the three values obtained for k_H are essentially identical, i.e.,

$$k_H = (2.0_2 \pm 0.0_1) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1} \text{ at } 20\ °\text{C}$$

(b) Competitive Study of Para-Substituted Styrenes. To gain insight into the nature of the transition state for addition of perfluoroalkyl radicals to alkenes, a competitive study was carried out using a series of para-substituted styrenes. The experimental procedure was essentially identical to that employed to determine k_H with n-Bu_3SnH (reaction 6). The measured k_H/k_{add} ratios



(6)

Table II. Competitive Kinetic Data for the Reactions of the Perfluoro-*n*-octyl Radicals with *n*-Bu_3SnH and Three Styrenes at 298 ± 2 K

styrene	k_H/k_{add}	k_{add}(LFP)/ 10^7 M^{-1} s^{-1} [a]	k_H/ 10^8 M^{-1} s^{-1} [b]
2. α-methylstyrene	2.27	8.9_3	2.0_3
3. styrene	4.40	4.6_2	2.0_3
4. 4-(trifluoromethyl)styrene	8.26	2.4_3	2.0_1

[a] From Table I. [b] Calculated from $(k_H/k_{add})k_{add}$.

Table III. Competitive Kinetic Data for the Reactions of Perfluoro-*n*-octyl Radicals with *n*-Bu_3SnH and Some Alkenes at 298 ± 2 K

alkene [IP (eV)][a]	k_H/k_{add}	k_{add}/ M^{-1} s^{-1} [b]	k_{add}^{rel}	σ[c]
14. 4-methoxystyrene [7.99][d]	3.12	6.5×10^7	1.41	–0.28
15. 4–methylstyrene [8.10]	3.31	6.1×10^7	1.33	–0.14
3. styrene [8.43]	4.40	4.6×10^7	1.00	0
16. 4-chlorostyrene [8.47][d]	5.69	3.6×10^7	0.77	0.24
4. 4-(trifluoromethyl)styrene	8.26	2.5×10^7	0.53	0.54
17. $H_2C{=}C(CH_3)CN$ [10.34]	63.0	3.2×10^6	0.072	
13. $H_2C{=}CHCN$ [10.91]	100	2.0×10^6	0.043	

[a] IPs as from footnote *c* in Table I, unless otherwise noted. [b] Calculated from $(k_{add}/k_H)k_H$. [c] Taken from ref 31. [d] Calculated IPs taken from ref 40.

were used to obtain the addition rate constants k_{add} (see Table III). The latter were then employed in a correlation of the reactivities of the styrenes toward perfluoroalkyl radicals using Hammett σ constants.[31] An excellent correlation with σ_p was obtained (*vide infra*).

(c) **Other Competitive Studies.** The ratios k_H/k_{add} were also obtained for the reaction of *n*-$C_8F_{17}^•$ with acrylonitrile, viz., 100, and with methacrylonitrile, viz., 63.0 (see Table III). These ratios were combined with $k_H = 2.0_2 \times 10^8$ M^{-1} s^{-1} (*vide supra*) to obtain k_{add} for these two substrates. The value obtained in this way for reaction of the *n*-$C_8F_{17}^•$ radical with acrylonitrile, viz., 2.0×10^6 M^{-1} s^{-1}, is in good agreement with that measured directly for the *n*-$C_7F_{15}^•$ radical, viz., 1.6×10^6 M^{-1} s^{-1}. These k_{add} values have been included in the addition rate constant/alkene vs IP correlation discussed below.

Discussion

Addition Reactions. Perfluoro-*n*-alkyl radicals are highly reactive in addition to alkenes with rate constants ranging from 9.4×10^7 M^{-1} s^{-1} for the pentafluoroethyl radical reacting with (electron-rich) α-methylstyrene to 1.6×10^6 M^{-1} s^{-1} for addition of the perfluoro-*n*-heptyl radical to (electron-deficient) acrylonitrile. The high reactivity of perfluoroalkyl radicals toward electron-rich olefins is further illustrated by comparison of the rates of addition of $R_f^•$ versus $R^•$ to terminal alkenes, see Table I.

In comparing $C_2F_5^•$ with *n*-$C_3F_7^•$, we would expect the extra *β-fluorine* substituent in $C_2F_5^•$ to provide greater electron-withdrawing power than the CF_3 group (which has a similar group electronegativity) in *n*-$C_3F_7^•$ due to the β-fluorine atom's ability to withdraw electron density via negative hyperconjugation (i.e., the stabilizing interaction of the SOMO orbital with the β-C–F σ* orbital.)[32,33] Consistent with these expectations as to relative electrophilicities, the perfluoro*ethyl* radical, $C_2F_5^•$, was found to be somewhat more reactive than *n*-$C_3F_7^•$ (see Table I). There is little or no difference in the rates of addition of *n*-$C_3F_7^•$, *n*-$C_7F_{15}^•$, and *n*-$C_8F_{17}^•$ to alkenes (see Tables I and III). Thus it seems likely that the reactivities of *all* homologous perfluoro-*n*-alkyl radicals can be defined by the reactivities of the *n*-$C_3F_7^•$, *n*-$C_7F_{15}^•$, or *n*-$C_8F_{17}^•$ radicals.

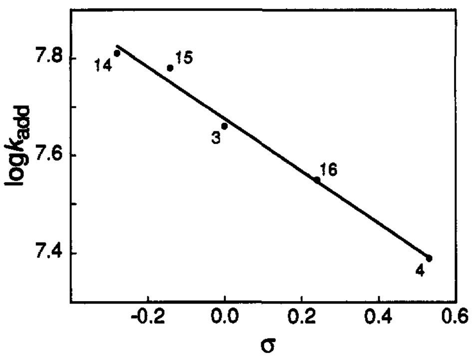


Figure 2. Plot of the log of the rate constants for addition of perfluoro-*n*-octyl radicals to some para-substituted styrenes (see Table III) vs Hammett σ values of the substituents. The correlations with σ^+ and $\sigma^•$ were not as good.

Although the electrophilicities of perfluoroalkyl radicals are probably the dominant factor giving rise to their high reactivities, there are a number of other potential factors which should also be considered:

(i) To the extent that *steric* effects might be involved, they would serve only to diminish the reactivities of perfluoroalkyl radicals relative to their *n*-alkyl counterparts since, although fluorine is a small substituent, it is certainly larger than a hydrogen atom.

(ii) Of probable relevance is the significantly stronger (*ca.* 11 kcal/mol)[23] C–C bond which forms when $R_f^•$ vs $R^•$ adds to an alkene. The greater exothermicity of the perfluoroalkyl radical addition reactions can be expected to lower the activation energies for these reactions relative to alkyl radical additions. "Extra" strong bonds are also formed when phenyl radicals[34] and cyclopropyl radicals[35] add to alkenes, and this factor has been considered to be relevant with respect to the greater reactivities of these two radicals relative to "ordinary" alkyl radicals.[34,35]

(iii) Of potential relevance is the "bent" σ-nature of perfluoro-*n*-alkyl radicals.[32,36,37] These radicals have nearly identical α-F hyperfine couplings (a^{19F} = 86–90 G) in their ESR spectra,[36,37] which implies that the extent of nonplanarity at their radical centers is very similar. In contrast, methyl is a planar π-radical. However, substantial bending (14–15° from planarity) is apparently required in the transition state for methyl radical addition to alkenes.[11] The energy cost for accomplishing this degree of pyramidalization has been calculated to be about 2.6 kcal/mol.[38] A nonplanar perfluoroalkyl radical might therefore be expected to have an inherent energetic advantage over a planar methyl radical in addition reactions.

The electrophilic character of *n*-perfluoroalkyl radicals was confirmed in the reactions of the *n*-$C_8F_{17}^•$ radical with a series of para-substituted styrenes. The log of the rate constants, k_{add}, given in Table III correlated extremely well with Hammett σ values, ⟨*r*⟩ = 0.99, as shown in Figure 2. The ρ value (slope) is negative (–0.53),[39] as would be expected for an electrophilic

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[31] Values of σ were taken from: Wayner, D. D. M. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 2, Chapter 21.

[32] Krusic, P. J.; Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 230–232.

[33] Stock, L. M.; Wasielewski, M. R. *Prog. Phys. Org. Chem.* **1981**, *13*, 253–313.

[34] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609–3614.

[35] Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877–4881.

[36] Meakin, P.; Krusic, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 8185–8188.

[37] Chen, K. S.; Krusic, P. J.; Meakin, P.; Kochi, J. K. *J. Phys. Chem.* **1974**, *78*, 2014–2030.

[38] Pacansky, J. *J. Phys. Chem.* **1982**, *86*, 485–488.

[39] For comparison relative rates of addition of $CCl_3^•$ radicals to a number of meta- and para-substituted styrenes at 80 °C yielded $\rho(\sigma)$ = –0.43 and $\rho(\sigma^+)$ = –0.42.[40]

[40] Sakurai, H.; Hayashi, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945–1949.

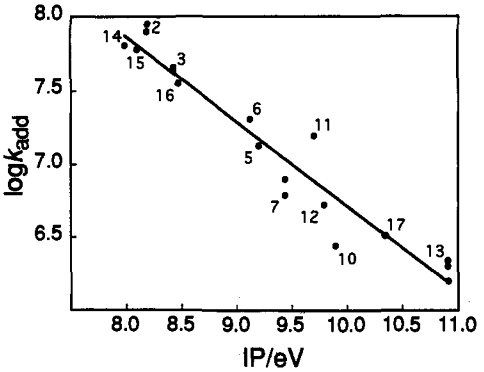
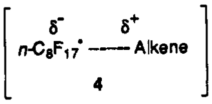


Figure 3. Plot of the log of the rate constants for addition of prototypical perfluoro-*n*-alkyl radicals (n-$C_3F_7^•$, n-$C_7F_{15}^•$, or n-$C_8F_{17}^•$) to some alkenes vs the ionization potentials of the alkenes (see Table I and Table III). Where there is more than one point per alkene, it is because rate constants were determined for more than one of the radicals mentioned above.

reactant.[41] These results imply that polar factors play some role in determining the rates of addition to the styrenes (and probably also to the other alkenes). Polarization tends to stabilize an early transition state (**4**) in which little radical character has been transferred to the substrate alkene.



$$\left[\overset{\delta^-}{n\text{-}C_8F_{17}^{\bullet}}\text{ —— }\overset{\delta^+}{\text{Alkene}}\right]$$

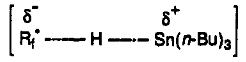
4

As indicated earlier, Fischer et al. have shown that the rates of addition to alkenes of the nucleophilic *tert*-butyl radical (with its high-lying SOMO) can be correlated with the electron affinities (EAs) of the alkenes,[6,18] which provide a measure of the alkene's LUMO energies. As the LUMO energy decreased, the rates of addition increased because the gap between the SOMO and the LUMO decreased. It is clear that the SOMO–LUMO interaction is dominant for *tert*-butyl radical addition to olefins.

The electrophilic perfluoro-*n*-alkyl radical, which one can assume to have a low-lying SOMO, would be expected to show a dominant SOMO–HOMO interaction in its additions to alkenes. That is, if steric hindrance is equivalent for a series of alkenes, the rates of addition of $R_f^•$ would be expected to correlate with the alkene IPs (which should reflect HOMO energies). As Figure 3 indicates, there is indeed a respectable correlation between log k_{add} for prototypical perfluoro-*n*-alkyl radicals (n-$C_3F_7^•$, n-$C_7F_{15}^•$, or n-$C_8F_{17}^•$) and terminal alkene IPs ($\langle r \rangle = 0.97$). This correlation is even better than Fischer and co-workers' correlation of *tert*-butyl radical additions to alkenes with the alkenes' EAs ($\langle r \rangle = 0.89$).[18] In both systems there are substantial deviations from the best straight line, which indicates that additional factors must be involved in determining the reaction rates.[42] Nevertheless, these two correlations serve to confirm the electrophilic character of perfluoro-*n*-alkyl radicals[43] and the nucleophilic character of the *tert*-butyl radical.

For steric reasons, the nonterminal olefins, β-methylstyrene, and cyclohexene are noticeably less reactive than might have been anticipated from their IPs. The lower reactivity of **9** relative to **10** is a reflection of the general observation that radicals add less readily to acetylenes than to olefins.

H-Abstraction from *n*-Bu$_3$SnH. In their reactions with tin hydride, the perfluoro-*n*-alkyl radicals are about 100 times as reactive as *n*-alkyl radicals at 20 °C. That is, for n-$R_f^•$, $k_H = 2.0_2 \times 10^8$ M^{-1} s^{-1}, and for n-$R^•$, $k_H = 2.0_7 \times 10^6$ M^{-1} s^{-1}.[44] Such a large rate enhancement is consistent with a polar transition state (**5**) which would "suit" both the electronegative $R_f^•$ radical and the electropositive Sn atom.



$$\left[\overset{\delta^-}{R_f^{\bullet}}\text{ —— H —— }\overset{\delta^+}{\text{Sn}(n\text{-Bu})_3}\right]$$

5

Summary

Absolute rate constants for the addition of perfluoro-*n*-alkyl radicals to alkenes and for the abstraction of hydrogen from *n*-Bu$_3$SnH have been measured in solution at room temperature. The perfluoro-*n*-alkyl radicals are more reactive than *n*-alkyl radicals in both types of processes. This enhanced reactivity is attributed mainly to the high electrophilicities of the perfluoro-*n*-alkyl radicals and in the addition reactions also to the greater exothermicity of the C–C bond forming process.[23] The rates of addition of $R_f^•$ radicals to terminal alkenes can be correlated with the IPs of the alkenes, indicating that polar effects (SOMO–HOMO interactions) are important in determining the rates of these reactions. It is anticipated that studies currently in progress on partially fluorinated *n*-alkyl radicals will shed more light upon the unique reactivity characteristics which have been uncovered thus far for the perfluoro-*n*-alkyl radicals.

Experimental Section

Time-Resolved Laser Flash Photolysis. The apparatus and procedures have been described in detail elsewhere.[29,45] The rate constants for the reactions which resulted in the formation of the benzylic radicals (reaction 2) were determined from the experimental growth curves of the absorption at ca. 320 nm measured over a range of substrate concentrations, according to eq I. Rate constants for the olefins and an acetylene which do not form easily observed products were obtained using 0.11 M β-methylstyrene as a spectroscopic "probe"[29] according to eq II. For the "probe" measurements of the rates for relatively unreactive substrates, where the addition of the substrate exceeded 5% of the total volume of the sample, eq V was used, with k_0' being corrected in each measurement for the "probe" concentration change.

$$k_{\text{exptl}}(320\text{ nm}) - k_0' = k_{\text{g}}[\text{substrate}] \qquad \text{(V)}$$

Preparation of Perfluorodiacyl Peroxides. Perfluorodipropionyl, perfluorodibutyryl, and perfluorodioctanoyl peroxides were prepared as solutions in Freon 113 from their respective acyl chlorides and purified using the procedure of Zhao et al.[28] Determination of yield and concentration of the peroxides was accomplished by iodometry, and the solutions were preserved until needed at −78 °C. ^{19}F NMR analysis indicated a purity of >95%. For perfluorodibutyryl peroxide: ^{19}F NMR (in Freon 113) δ −80.91 (3F, t, J = 8.4 Hz), −117.28 (2F, q, J = 7.9 Hz), −127.06 (2F, s).

General Procedure for Competition Experiments. All experiments were carried out in sealed quartz NMR tubes, which were degassed through several freeze–thaw cycles and sealed under vacuum. The styrenes were passed through silica gel before use. A stock solution was prepared by adding 105.3 mg (0.194 mmol) of n-$C_8F_{17}I$ and 20 μL (0.164 mmol) of (trifluoromethyl)benzene (internal standard) to 1.5 mL of benzene-d_6. The solvent for all the NMR measurements was C_6D_6, and chemical shifts are reported as δ upfield from TMS for ^{1}H and ^{13}C NMR and from $CFCl_3$ for ^{19}F NMR.

To 250 μL of this stock solution in a quartz NMR tube were added 80 μL (0.298 mmol) of n-Bu$_3$SnH and either 25, 50, 100, 200, or 400 μL of a styrene. The tube was degassed by three freeze–thaw cycles and sealed under vacuum. The solutions were irradiated by UV light at room temperature for 1 h, after which they were analyzed quantitatively by

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[41] For numerous examples of negative ρ values for Hammett correlations for relative rates involving H-atom abstractions from a wide variety of substituents by electrophilic radicals, see: Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 7.

[42] A referee has pointed out that the three olefins containing strongly electron-attracting groups (i.e., 11, 13, and 17) are more reactive than would be predicted from the overall correlation and that this may indicate an interplay of polar and enthalpy effects. If these three olefins are ignored, the correlation between log k_{add} and IP improves slightly ($\langle r \rangle = 0.98$).

[43] Certainly these radicals show no sign of being ambiphilic over the range of alkenes investigated.

[44] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

[45] Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430–4435.

^{19}F NMR to determine the relative amounts of reduction product, *n*-$C_8F_{17}H$ (CF_2H signal at −137.6), and styrene adduct, *n*-$C_8F_{17}CH_2CH(CH_3)C_6H_5$ (CF_2CH_2- signal (AB) at −112.5 and −114.5), *n*-$C_8F_{17}CH_2CH_2C_6H_5$ (CF_2CH_2- at −114.6), or *n*-$C_8F_{17}CH_2CH_2(4\text{-}CF_3C_6H_4)$ (CF_2CH_2- at −114.7), and to determine the absolute yields using the (trifluoromethyl)benzene as internal standard (CF_3 signal at −63.5).

Preparation of α-Methylstyrene Adduct, *n*-$C_8F_{17}CH_2CH(CH_3)C_6H_5$. To 1 g (2.0 mmol) of *n*-$C_8F_{17}Br$ in 10 mL of benzene in a 25-mL, thick-walled Pyrex tube were added 1.16 g (2.0 mmol) of *n*-Bu_3SnH, 7.08 g (60 mmol) of α-methylstyrene, and 12 mg of AIBN. The tube was degassed by three freeze–thaw cycles and sealed under vacuum, after which the tube was heated at 60 °C for 8 h. An NMR of the crude reaction product indicated 85.8% yield of the adduct, which after distillation and column chromatography (silica gel, $CHCl_3$/*n*-hexane (1:1)) provided 0.65 g (60.4% yield) of *n*-$C_8F_{17}CH_2CH(CH_3)C_6H_5$ (GC purity in excess of 98%): bp 60–63 °C/0.01 mmHg; ^{1}H NMR δ 7.35–7.19 (5H, m), 3.25 (1H, sex, J = 7 Hz), 2.20–2.50 (2H, m), 1.39 (3H, d, J = 7.2 Hz); ^{19}F NMR δ −81.41 (3F, m, J = 9.7 Hz), −112.54 and −114.52 (AB, 2F, $^2J_{FF}$ = 268 Hz), −122.08 (2F, m), −122.37 (4F, m), −123.20 (2F, m), −124.07 (2F, m), −126.67 (2F,m); ^{13}C NMR δ 22.7 (CH_3), 33.1 (CH), 38.4 (CH_2F_2, t, J = 21.2 Hz), 126.6, 126.7, 126.8, 145.7 (aromatic); MS (EI) (*m/e*, relative intensity), 528 (M^+) 23, 523 (15), 105 (100).

Preparation of Reduction Product, *n*-$C_8F_{17}H$. To a solution of 1 g (2.0 mmol) of *n*-$C_8F_{17}Br$ in 5 mL of THF in a 15-mL Pyrex tube were added 0.7 g (2.4 mmol) of *n*-Bu_3SnH and 12 mg of AIBN. After three freeze–thaw–pump cycles and sealing under vacuum, the mixture was heated at 60 °C for 4 h. The crude reaction mixture was taken up in ether, washed with water, dried, and distilled to give 0.65 g (77.5% yield) of *n*-$C_8F_{17}H$: bp 112 °C, ^{1}H NMR δ 7.35 (1H, t of t, $^2J_{HF}$ = 52.0 Hz, $^3J_{HF}$ = 5.0 Hz); ^{19}F NMR δ −81.41 (3F, t, J = 9.8), −122.50 (4F, m), −123.23 (2F, m), −123.78 (2F, m), −126.70 (2F, s), −129.80 (2F, s), −137.57 (2F, t, J_{HF} = 51.9 Hz); ^{13}C NMR δ 107.6 (t, CF_2H, J = 250 Hz); HRMS calcd for *n*-$C_8F_{17}H$ 419.9807, found 419.9805; MS (EI) (*m/e*, relative intensity), 420 (M^+) (1.8), 419 (28), 219 (26), 181 (15), 169 (63), 131 (100), 119 (50).

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Supplementary Material Available: Tables IV–XXIX giving detailed data for the LFP and competitive kinetic experiments (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.