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Perfluoro-*tert*-Butyl, a Reactive, Neutral, Electrophilic Carbon-Centered Radical *par Excellence.*[1]

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Abstract: Absolute rate constants for $(CF_3)_3C^\bullet$ addition to terminal olefins increase by roughly a factor of 30 for every 1 eV decrease in the ionization potential (IP) of the alkene. A similar decrease in IP increases the rate of addition of $CF_3^\bullet$ and n-$C_3F_7^\bullet$ by a factor of only 3 or 4. The perfluoro-*tert*-butyl radical is, therefore, the most electrophilic, neutral carbon-centered radical to have been studied to date.
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We recently reported on the existence of a strong synergistic effect of perfluorination on the absolute rate constants for addition of *n*-alkyl radicals to three styrenes in solution at room temperature.[3] For example, the relative rates of addition to styrene of $RCH_2CH_2CH_2^\bullet$, $RCF_2CH_2CH_2^\bullet$, $RCH_2CF_2CH_2$, $RCH_2CH_2CHF^\bullet$, $RCH_2CH_2CF_2^\bullet$, and $RCF_2CF_2CF_2^\bullet$ are 0.92 : 1.0 : 4.0 : 3.5 : 21 : 330, respectively. That is, γ-fluorination has essentially no effect on reactivity and two β-fluorines increase reactivity by a factor of four. One α-fluorine increases reactivity by 3.5 but two α-fluorines increase reactivity by 21 rather than by $(3.5)^2 = 12$. Furthermore, perfluorination increases reactivity by 330 rather than by 4(2 β-F) x 21 (2 α-F) = 84. Thus, so far as radical reactivity is concerned, the effect of perfluorination is clearly much more than the sum of its parts. As we had pointed out previously[4,5] the dominant factor giving rise to the high reactivities of perfluoro-*n*-alkyl radicals in their additions to alkenes, particularly electron-rich alkenes,[4,5] is the high electrophilicities of these neutral but very electron-deficient radicals. That is, charge transfer interactions stabilize an early transition state and lower both the enthalpic and entropic[6] barriers to reaction 1 and, consequently, the reaction rate is increased. Consistent with this concept, the absolute rate constants for addition of perfluoro-*n*-alkyl radicals to alkenes, $k_{add}^{n\text{-}C_nF_{2n+1}}$, decreased as the ionization potential (IP) of the alkenes increased.[3-5] Indeed, a plot of $\log\left(k_{add}^{n\text{-}C_nF_{2n+1}}/M^{-1}\,s^{-1}\right)$ for addition to thirteen 1-substituted and 1,1-disubstituted ethylenes gave an excellent straight line for olefins ranging from

4-methoxystyrene (IP = 7.99 eV, $k_{add} = 6.5 \times 10^7$ M^{-1} s^{-1}) to acrylonitrile (IP = 10.91 eV, $k_{add} = 1.6 \times 10^6$ M^{-1} s^{-1}).[5]

$$RF\bullet + H2C{=}C(R')R'' \longrightarrow \left[(RF\bullet)\delta\text{-}\ (H2C{=}C(R')R'')\delta{+}\ \right]\ddagger \longrightarrow R_F CH_2\dot{C}(R')R'' \quad (1)$$

The perfluoro-*tert*-butyl group is, inductively, more strongly electron withdrawing than a perfluoro-*n*-alkyl or trifluoromethyl group. For example,[7] the Hammett σ_m constants are 0.55, 0.44 and 0.43 for $(CF_3)_3C$—, $CF_3CF_2CF_2$—, and CF_3—, respectively, and the corresponding *F* (field / inductive) values are 0.53, 0.42 and 0.38, respectively.[8] These data suggested that transition state stabilization due to polar effects in addition reactions of $CF_3^\bullet$ would be rather similar to those found previously for $n\text{-}C_nF^\bullet_{2n+1}$ and that polar effects should be considerably greater for the $(CF_3)_3C^\bullet$ radical.[10]

The $CF_3^\bullet$ and $(CF_3)_3C^\bullet$ radicals were generated by 308 nm laser flash photolysis (LFP) of their parent iodides in Freon 113 at room temperature.[11] Rate constants for their additions to selected olefins were measured in the usual way[12] and are given in Table 1, together with some of our earlier kinetic data for addition of $n\text{-}C_3F_7^\bullet$ to these same olefins.[5] Plots of $\log(k_{add}\ /\ M^{-1}\ s^{-1})$ vs. IP of the olefins are shown for the three perfluorinated alkyl radicals in Figure 1. The least squares lines shown in this figure correspond to the following equations: [14]

$$\log\left(k_{add}^{CF_3}\ /\ M^{-1}\ s^{-1}\right) = 12.0 - 0.49\ IP\ /\ eV$$

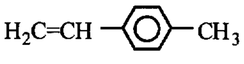
$$\log\left(k_{add}^{n\text{-}C_3F_7}\ /\ M^{-1}\ s^{-1}\right) = 12.5 - 0.56\ IP\ /\ eV$$

$$\log\left(k_{add}^{C(CF_3)_3}\ /\ M^{-1}\ s^{-1}\right) = 21.0 - 1.49\ IP\ /\ eV$$

The perfluoro-*tert*-butyl data stand as a nice contrast to Wu and Fischer's[15] kinetic data for addition of the strongly nucleophilic hydroxymethyl radical to terminal olefins which they correlated with the electron affinities (EA) of the alkenes,[16] viz., $\log\left(k_{add}^{HOCH_2}\ /\ M^{-1}\ s^{-1}\right) = 5.57 + 1.53\ EA\ /\ eV$.

The slopes of the lines shown in Figure 1 can be converted to dimensionless quantities by converting the abscissa to kcal / mol (1 eV = 23.06 kcal/mol) and the vertical axis to the free energy for reaction ($\Delta G_{add} = -2.3\ RT \log\left(k_{add}\ /\ M^{-1}\ s^{-1}\right) = -1.36 \log\left(k_{add}\ /\ M^{-1}\ s^{-1}\right)$ kcal / mol). Thus converted, the slopes of the three lines are 0.029, 0.033 and 0.088 for $CF_3^\bullet$, $n\text{-}C_3F_7^\bullet$ and $(CF_3)_3C^\bullet$, respectively. As would be expected

Table 1. Absolute Rate Constants for the Addition of Some Perfluoroalkyl Radicals to Selected Alkenes in Freon 113 at 298 ± 2 K, as Measured by LFP.

	k_{add} / 10^6 M^{-1} s^{-1} [a]		
Alkene (IP / (eV) [b]	$(CF_3)_3C^\bullet$	$CF_3^\bullet$	$CF_3CF_2CF_2^\bullet$ [c]
1.  [8.10]	740 ± 30	140 ± 20	130 ± 20 [d]
2. $H_2C{=}C(CH_3)C_6H_5$ [8.19] [e]	590 ± 60	87 ± 8	78 ± 8
3. $H_2C{=}CHC_6H_5$ [8.43]	370 ± 20	53 ± 6	43 ± 1
4. $H_2C{=}CHC_6F_5$ [9.20]	16 ± 1	26 ± 2	13 ± 1
5. $H_2C{=}C(CH_3)C(O)OCH_3$ [9.70]	3.8 ± 0.2	f	19 ± 1
6. $H_2C{=}CHCN$ [10.91]	g	4.4 ± 0.4	2.2 ± 0.1

[a] Errors correspond to 2 σ but include only random errors. [b] NIST Standard Reference Database 25. *NIST Structures Properties Database and Estimation Program 1991*; U.S. Department of Commerce: Gaithersberg, MD 20899, 1991. [c] From reference 5 unless otherwise noted. [d] Measured in this work. [e] 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. [f] Not measured. [g] Too slow to measure.

on the basis of their σ_m and F values (*vide supra*) the $CF_3^\bullet$ and n-$C_3F_7^\bullet$ additions are, roughly, equally subject to polar effects and the $(CF_3)_3C^\bullet$ radical additions are much more strongly influenced by the IP of the olefin.[18] However, the dimensionless slopes serve to emphasize the fact that even with the $(CF_3)_3C^\bullet$ radical only ca. 9% of a change in the ionization energy of the olefin substrate is reflected in the change in free energy for the addition reaction. Nevertheless, perfluoro-*tert*-butyl is by far the most electrophilic, neutral, carbon-centered radical for which rate constants for addition to olefins have been determined.

We have previously pointed out[5] that although the electrophilicities of perfluoroalkyl radicals are probably the dominant factor giving rise to their high reactivities, there are three other potential factors which should be considered:

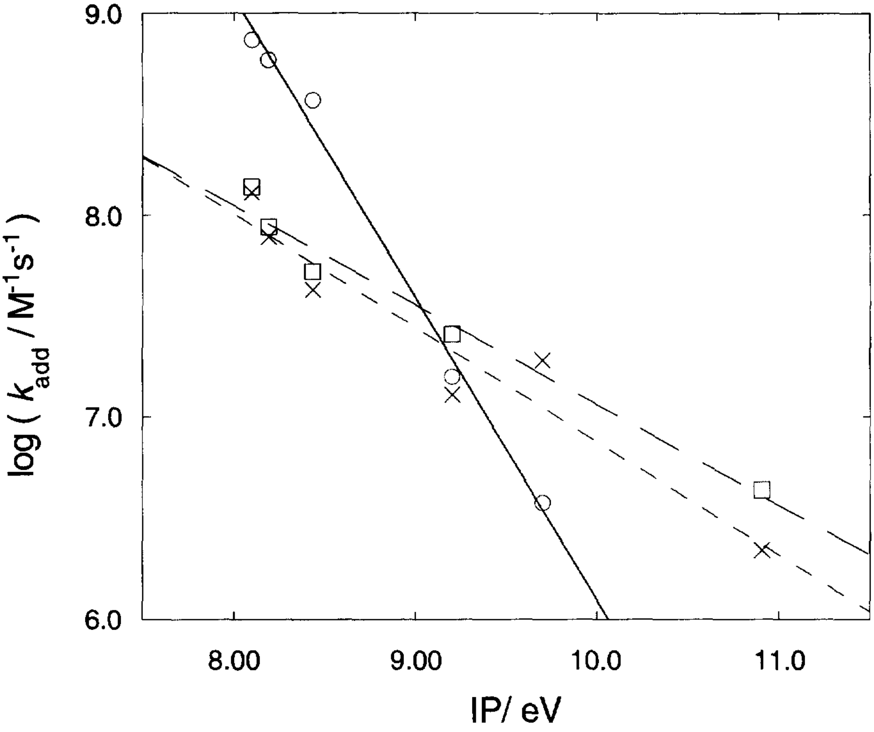


Figure 1. Plot of $\log(k_{add} / M^{-1}\ s^{-1})$ vs. IP of the alkenes. The data are from Table 1: $(CF_3)_3C^{\bullet}$, ○ ; $CF_3^{\bullet}$, □ ; n-C_3F_7, ×.

(i) Steric effects might diminish the reactivities of perfluoroalkyl relative to alkyl radicals.

(ii) The stronger C—C bond formed when $R_F^{\bullet}$ adds to an alkene relative to $R^{\bullet}$ (ca. 11 kcal / mol).

(iii) The non-planar ("bent") σ-nature of perfluoro-*n*-alkyl radicals and the $CF_3^{\bullet}$ radical might be expected to give these radicals an inherent energetic advantage over planar (π) alkyl radicals in addition reactions since there is no energy cost to reach the degree of bending required in the transition state (estimated to be 1.6 and 1.5 kcal / mol for methyl and *tert*-butyl radical additions to ethylene, respectively).[19]

The high reactivity of perfluoro-*tert*-butyl implies that steric effects are minimal in these addition reactions, i.e., factor (i) is relatively unimportant. More interestingly, the $(CF_3)_3C^{\bullet}$ radical is known to be a planar, π-radical,[20] which indicates that factor (iii) is also relatively unimportant. This radical is more resistant to pyramidalization than the *tert*-butyl radical[20b,21] and, indeed, INDO calculations show that even a 10° out-of-plane deformation requires ca. 4 kcal / mol in energy.[20c] Presumably the high electron affinity of $(CF_3)_3C^\bullet$ and consequent partial electron transfer from electron-rich olefins in the transition state mixes sufficient $(CF_3)_3C$ anion character into the radical that pyramidalization is without significant energy cost and hence rates of addition are high.

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7. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Revs.* **1991**, *91*, 165-195.
8. Similarly, there is a dramatic decrease in C—H acidities along the series $(CF_3)_3CH$, $CF_3(CF_2)_nCF_2H$, CF_3H for which the pK_a values are:[9a] 11 (or 20)[9b], 30 and 31, respectively.
9. (a) Andreades, S. *J. Am. Chem. Soc.* **1964**, *86*, 2003-2010. (b) Holz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 1-74.
10. For a gas phase study of the rates of addition of perfluoroalkyl radicals to $CH_2{=}CHF$ and $CH_2{=}CF_2$ relative to $CH_2{=}CH_2$, see: Tedder, J. M.; Walton, J. C.; Vertommen, L. L. T. *J. Chem. Soc., Faraday Trans. 1*, **1979**, *75*, 1040-1049.
11. We have previously demonstrated[5] that the measured rate constants for addition to β-methylstyrene of $C_2F_5^\bullet$ radicals generated by LFP of C_2F_5I and of $(C_2F_5CO_2)_2$ are essentially equal.
12. For the styrenes the growth of the benzylic radical was monitored directly at ~ 320 nm. β-Methylstyrene (0.11 M) was used as a spectroscopic "probe"[5,13] for methyl methacrylate and acrylonitrile which do not yield easily observed product radicals.
13. Paul, H.; Small, R. D.; Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520-4527.

14. We have previously reported kinetic data for the addition of $n\text{-}C_3F_7^\bullet$ to six olefins which are not listed in Table 1 (see ref. 5). The equation obtained using the kinetic data for all 12 olefins is:

$$\log(k_{\mathrm{add}}^{n\text{-}C_3F_7} / \mathrm{M^{-1}\,s^{-1}}) = 12.7 - 0.60\ \mathrm{IP / eV}$$

15. Wu, J. Q.; Fischer, H. *Int. Chem. Kinet.* **1995**, *27*, 167-179.

16. No apparent correlation was found between $\log\left(k_{\mathrm{add}}^{\mathrm{HOCH_2}} / \mathrm{M^{-1}\,s^{-1}}\right)$ and the overall reaction enthalphy.[15] In contrast, similar kinetic data for the cyanomethyl ($NCCH_2^\bullet$),[17a] (*tert*-butoxy)-carbonylmethyl ($Me_3COCOCH_2^\bullet$),[17a] benzyl ($PhCH_2^\bullet$)[17b] and cumyl ($PhCMe_2^\bullet$)[17b] correlate well with the overall reaction enthalpies, with only minor polar effects.

17. (a) Wu, J. Q.; Beranek, I.; Fischer, H. *Helv. Chim. Acta* **1995**, *78*, 194-214.
    (b) Walbiner, M.; Wu, J. Q.; Fischer, H. *Helv. Chim. Acta* **1995**, *78*, 910-924.

18. The $(CF_3)_2CF$- group has $\sigma_m = 0.37$ and $F = 0.31$. Neither of these values correlate with the expected monotonic trend in these quantities along the series CF_3-, CF_3CF_2- ($\sigma_m = 0.47$, $F = 0.44$), $(CF_3)_2CF$-, $(CF_3)_3C$, nor do they fit with the known monotonic trend in C—H acidities along this series (pK_a $(CF_3)_2CFH = 20$).[8,9] For the $(CF_3)_2CF^\bullet$ radical, a two point (styrene, $k_{\mathrm{add}} = 1.2 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$; $C_6F_5CH{=}CH_2$, $k_{\mathrm{add}} = 8.1 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$) plot gives a dimensionless slope of 0.090. There is thus a clear implication that this radical is more like $(CF_3)_3C^\bullet$ than like the $CF_3^\bullet$ or $n\text{-}C_3F_7^\bullet$ radical. It seems probable that the σ_m and F values for the perfluoroisopropyl group have been underestimated.

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21. Out-of-plane bending of the *tert*-butyl radical is governed by a double minimum potential function[22] and pyramidalization is relatively facile.

22. See, e.g., Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978** *100*, 6750-6752. Schrader, B.; Pacansky, J.; Pfieffer, U. *J. Phys. Chem.* **1984**, *88*, 4069-4073. Paddon-Row, M. N.; Houk, K. N. *J. Phys. Chem.* **1985**, *89*, 3771-3774.

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