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Reactivity of Perfluoro-*n*-alkyl Radicals
A Hammett Study of Hydrogen Transfer from Arene Thiols

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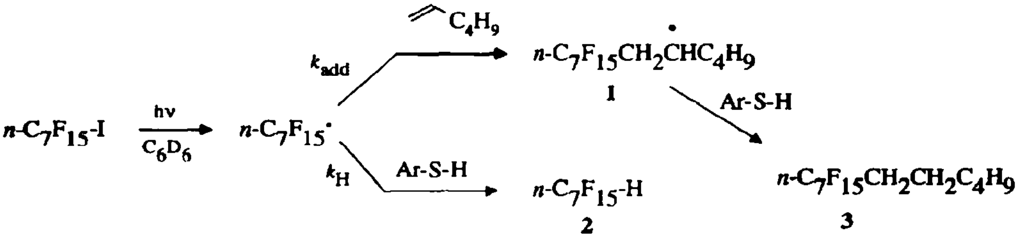
Abstract: A Hammett study of hydrogen atom abstraction by the perfluoro-*n*-heptyl radical is presented. Excellent correlation of the rates with σ^+, with a ρ^+ value of -0.56, provides important corroboration of the substantial influence of transition state polar effects on this unexpectedly slow process.

In a series of recent papers, we have reported that perfluoro-*n*-alkyl radicals generally exhibit a significantly enhanced reactivity when compared to their hydrocarbon counterparts.[1-3] Such enhanced reactivity has been observed for both addition reactions to alkenes (i.e., addition to α-methylstyrene >1300 times faster)[2] and hydrogen abstractions from silanes and stannanes (i.e., reduction by Et_3SiH >800 times faster).[3]

Undoubtedly a significant portion of such enhancement can be attributed to the fact that such reactions are considerably more exothermic for fluorinated versus hydrocarbon radicals.[4] Also pertinent is the fact that σ-radicals are more reactive than π-radicals.[5] Nevertheless, that this cannot be the whole story was demonstrated by our observation that reduction of perfluoro-*n*-heptyl radical by benzene thiol occurs at a rate >400 times *slower* than the analogous reduction of an *n*-alkyl radical.[3,6] Thus while benzene thiol reduces alkyl radicals at a rate 50 times greater than *n*-Bu_3SnH,[6] it reduces perfluoro-*n*-alkyl radicals at a rate >700 times *slower* than *n*-Bu_3SnH. This huge differential reactivity has been attributed to the important contribution of *polar effects* in the transition states for such hydrogen transfer reactions, and to the fact that alkyl radicals and perfluoroalkyl radicals have essentially opposite polar character, the former being nucleophilic while the latter are highly electrophilic.

In order to provide corroboration for the role of polar effects in such reactions, a Hammett study was carried out for the reduction of *n*-$C_7F_{15}I$ by a series of arene thiols.



The abstraction of hydrogen from arene thiols by perfluoro-*n*-alkyl radicals is a very exothermic process [for: $R_f^{\bullet} + C_6H_5SH \rightarrow R_f\text{-}H + C_6H_5S^{\bullet}$, $\Delta H° = -24$ kcal/mol],[4] and the activation energy for this reaction must be very low (i.e., ≤ 3 kcal/mol).[6] With such an energy profile, the [7] reaction should have a reactant-like transition state, with little bond-breaking and little transfer of radical character to the thiyl site. It is for such transition states that FMO interactions and polarization effects would be expected to play their most important role.

Indeed it can be seen from the data in the Table that there is a definite relationship between the rates of reduction and the "electron-richness" or "-poorness" of the arene thiol, with the electron-rich *p*-methoxy derivative being 5.5 times more reactive than the most electron-poor *p*-CF_3 derivative.

Table I. Rates of H-Atom Abstraction from Arene thiols at 30 °C in C_6D_6 [a]

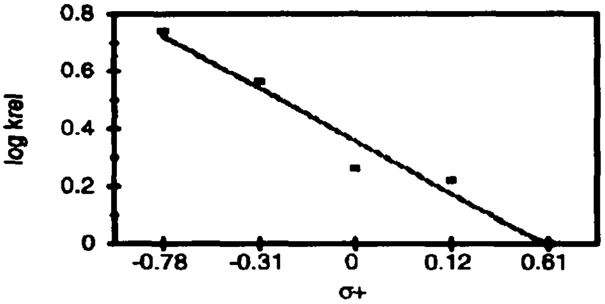
Aryl Subst.	*p*-OCH_3	*p*-CH_3	H	*m*-OCH_3	*p*-CF_3
$k_H/10^5\ M^{-1}s^{-1}$	9.9 (±0.9)	6.6 (±0.6)	3.3 (±0.3)	3.0 (±0.3)	1.8 (±0.2)
σ^{+b}	-0.78	-0.31	0	+0.12	+0.61

[a] All reductions were run in 1:1 ArSH/C_6D_6; [b] Ref. 8

In a related study of the hydrogen abstraction from arene thiols by the similarly electrophilic *t*-butoxyl radical, the best correlation of the rates with Hammett substituent constants was found to be with σ^+.[9] Likewise, a Hammett plot of our data in Table 1 versus σ^+ provided the good correlation shown in Fig. 1, and a ρ^+ value of -0.56 (r = 0.986), which compares with the value of - 0.30 (r = 0.987) which was observed for *t*-butoxyl. Much poorer correlations were obtained when the Log k_{rel}'s were plotted against either σ or $\sigma^{\bullet}$.

Figure 1

Hammett Plot of Arene Thiol Rates



The observed results are consistent with our experience that perfluoroalkyl radicals are electronegative, electron-accepting radicals which, in their reactions with H-atom donors as well as with alkenes prefer electropositive, electron-donating reac-tion partners. Silane and stannane hydrogen atom donors fulfill such a scenario very well and thus make excellent H-atom donors to perfluoroalky radicals. Benzene thiol, on the other hand, does not match-up as well, since benzene thiyl turns out to be quite an electronegative radical fragment.[10,11] In terms of polarization, this means that an ideal transition state for hydrogen-abstraction generates considerable negative charge at the perfluoroalkyl radical site and considerable positive charge at the incipient, H-donor, radical site. Incipient benzene thiyl is apparently reluctant to take on such positive charge.

In spite of the clear intervention of polarization effects, one still worries about concluding that polarization is the *sole* reason for R_f's unexpectedly slow rate of hydrogen abstraction from arene thiols, particularly since a diminution in rate does not seem to accrue from the similarly mismatched transition states for hydrogen transfer to the very electrophilic *t*-butoxyl radical. Unfortunately, the absolute rate of reaction of *t*-butoxyl with benzene thiol has not yet been reported. However, its rates of H-atom abstraction from phenol ($3.3 \times 10^8\ M^{-1}s^{-1}$) and substituted phenols have been measured and are among the fastest yet observed for *t*-butoxyl.[12] In our attempts to measure the rate of reduction of perfluoro-*n*-heptyl radical by phenol, it was found that aromatic addition processes competed with H-atom abstraction, thus making accurate rate measurements infeasible.

At this point, we can say that polarization is certainly *a* factor. Whether it is the only, or even the major, factor will be determined by future experiments. Hopefully, as we probe deeper into the various aspects of the reactivity of perfluoro- and *partially-fluorinated* radicals with arene thiols and other H-atom transfer agents, a more complete understanding of the factors which are involved in determining the rates will be obtained.

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7. In a typical experiment, a solution of perfluoro-*n*-heptyl iodide in benzene-d_6 was photolyzed in the presence of appropriate amounts of 1-hexene and arene thiol. The thus-generated n-$C_7F_{15}^{\cdot}$ radicals underwent competitive kinetically controlled reduction to form **2** or addition to 1-hexene to form intermediate radical **1** which was itself reduced to form adduct **3**. The ratio of **2**:**3** was determined directly by ^{19}F NMR analysis of the CF_2H peak (δ -138.1 ppm) of **2** versus the CF_2CH_2 peak (δ -114.4 ppm) of **3**. This ratio, obtained for varied concentrations of 1-hexene, combined with the respective ratios of 1-hexene to arene thiol and the known value for k_{add} for n-$C_7F_{17}^{\cdot}$ ($7.9 \times 10^8\ M^{-1}s^{-1}$ at ~298 °K) allowed the determination of the ratio k_H/k_{add} as has been described previously.[2,3]
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10. Absolute (Mulliken) electronegativities, χ, of radicals are defined by the following equation: $\chi = (IP + EA)/2$, and such values are available for a number of radicals,[11] unfortunately perfluoro-*n*-alkyl radicals not being among them. A typical "nucleophilic" radical, *t*-Bu˙, for example, has an χ value of 3.31 eV, while the values for $C_6H_5S^{\cdot}$ and $C_6H_5O^{\cdot}$ are 5.5 and 5.6 eV, respectively. χ for ˙OH is 7.5. One might realistically expect the value for $R_f^{\cdot}$ to lie between 5.5 and 7.5, while the values for $R_3Si^{\cdot}$ and $R_3Sn^{\cdot}$ should lie below that for *t*-Bu.
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