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Absolute rate constants for some hydrogen atom abstraction reactions by a primary fluoroalkyl radical in water†

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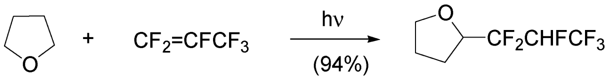
A combination of laser flash photolysis and competitive kinetic methods have been used to measure the absolute bimolecular rate constants for hydrogen atom abstraction in water from a variety of organic substrates including alcohols, ethers, and carboxylic acids by the perfluoroalkyl radical, $^{\bullet}CF_2CF_2OCF_2CF_2SO_3^- Na^+$. Comparison, where possible, of these rate constants with those previously measured for analogous reactions in the non-polar organic solvent, 1,3-bis(trifluoromethyl)benzene (*J. Am. Chem. Soc*, 1999, **121**, 7335) show that the alcohols react 2–5 times more rapidly in the water solvent and that the ethers react at the same rate in both solvents. A transition state for hydrogen abstraction that is more reminiscent of an "intimate ion pair" than a "solvent separated ion pair" is invoked to explain these modest solvent effects.

Introduction

Perfluoroalkyl radicals have unusual reactivity characteristics that derive largely from their great electrophilicity but also, in part, from their pyramidal geometry at the radical center and the thermodynamics of their reactions.[1–4] Thus, rate constants for hydrogen atom abstraction by perfluoroalkyl radicals from relatively electropositive atoms such as Sn, Si and even from carbon are much larger than those of the analogous alkyl radicals. For example, the rate constants for hydrogen abstraction from n-Bu_3SnH and Et_3SiH by n-$R_f^{\bullet}$ are 85 and 714 times larger, respectively, than by n-$R^{\bullet}$.[5–7]

Although the C–H bonds of simple functionalized or non-functionalized aliphatic organic compounds are effectively inert towards abstraction by alkyl radicals, perfluoroalkyl radicals are sufficiently reactive that they can efficiently propagate synthetically useful free radical chain reactions, such as the one depicted in overall terms below.[8]



Similarly, and as discussed by Shtarev *et al.*,[9] rate constants for the reactions of the n-octyl radical with THF and diethyl ether at 22 °C (4.9×10^2 and 1.2×10^2 M^{-1} s^{-1}, respectively)[10,11] are considerably lower than those for the n-$C_4F_9^{\bullet}$ radical, *viz.*,[7] 3.1×10^4 and 2.2×10^4 M^{-1} s^{-1}, respectively, in 1,3-bis(trifluoromethyl)benzene (BTB). These and many other rate constants were obtained *via* competition experiments in which the relative rates of H-atom abstraction from the substrates were determined *versus* deuterium abstraction from t-$BuSiMe_2D$ (for which $k_D = 1.49 \times 10^5$ M^{-1} s^{-1}).[9] This work indicated that the rate constants for H-atom abstraction by the n-$C_4F_9^{\bullet}$ radical depended on at least three factors: (i) the C–H bond dissociation enthalpy (BDE) (ii) steric effects and (iii) transition state polar effects. With regard to this last factor, it is worth noting that chloroalkanes are less reactive towards n-$C_4F_9^{\bullet}$ than alkanes[7] despite the fact that a chlorine atom lowers the C–H BDE at the carbon bearing the chlorine relative to the C–H BDE of the corresponding alkane. The electron-withdrawing Cl atom obviously destabilizes the "normal" polarized transition state for C–H abstraction by the electronegative n-$C_4F_9^{\bullet}$ radical (Fig. 1).

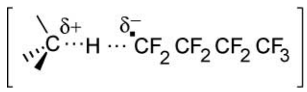


Fig. 1 Polar transition state for an H-atom abstraction.

Because of their high electrophilicities and the acknowledged importance of transition state polar effects on the reactivities of perfluoro-n-alkyl radicals in both hydrogen abstractions and alkene additions,[1–3] the rates of such reactions might be expected to be fairly strongly influenced by solvent polarity.[12] However, no attention appears to have previously been paid to this matter except in a footnote in one of our earlier publications reporting that $CF_3^{\bullet}$ and n-$C_3F_7^{\bullet}$ add to styrene ~3 times and to pentafluorostyrene ~1.5 times more rapidly in CH_3CN than in 1,1,2-trichloro-1,2,2-trifluoroethane (F113).[13] A broad investigation of absolute rate constants for the addition and hydrogen atom abstraction reactions of fluorinated alkyl radicals *in water* has recently been initiated.[14] Since the rate constants for many such reactions in non-polar organic solvents (F113, C_6D_6 and BTB) are available,[3,9] it will become possible to assess the significance of solvent effects on these reactions. In our initial study, absolute rate constants for the addition of the $^{\bullet}R_fSO_3Na$ radical (**1**, where R_f = $CF_2CF_2OCF_2CF_2$) radical to a series of water-soluble alkenes bearing carboxylate ion functionality in aqueous solution were measured by laser flash photolysis (lfp).[14] As was the case for our related studies in F113 it was concluded that thermodynamic, polar, and steric effects probably all played some role in the dynamics of these additions. In particular, rate constants in water, although nearing the diffusion limit, were all *larger* than those reported earlier for their structural counterparts in F113,[15] with rate enhancements of 3–9 fold. It was concluded that these enhancements in water *vs.* F113 most probably arose from a more effective stabilization of the polar transition state for addition in the more polar solvent.

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† Electronic supplementary information (ESI) available: Tables of kinetic data and plots of kinetic data. See http://www.rsc.org/suppdata/ob/b3/b313757k/

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In the present work, one of the alkenes examined in the earlier lfp study,[14] sodium 4-(1-propenyl)benzoate, **2** was used as a kinetic probe in further lfp experiments to obtain absolute rate constants for H-atom abstraction by the fluoroalkyl radical, **1**, from THF and isopropanol in water. The THF rate constant was then used in conjunction with competition experiments to determine absolute rate constants in water for hydrogen abstraction by **1** from a diverse range of substrates.

An understanding of structure–reactivity relationships and the influence of reaction medium on the kinetics of C–H abstraction by perfluorinated alkyl radicals has both scientific and practical relevance. The manufacture of industrial fluoropolymers typically requires the use of H-transfer agents to control molecular weight and molecular weight distributions under aqueous dispersion, suspension, or emulsion polymerization conditions.[16–18] Common chain-transfer agents[19,20] include chloroform, hydrocarbons, alcohols and more recently, ethers,[19] but the recipes for their use are entirely empirical and there have been no systematic, quantitative kinetic data on their reactivity toward model propagating fluorinated radicals in aqueous media to guide their use or the design of improved chain-transfer agents. This study provides the first set of such data.

Results

To obtain the absolute rate constants for hydrogen atom abstraction from organic substrates by the $^{\bullet}R_fSO_3^-$ radical in water, it was necessary to determine at least *one* such rate constant directly or indirectly *via* a laser flash photolysis (lfp). This lfp rate constant could then be used in conjunction with relative rate constants obtained from competition experiments to derive absolute rate constants for H-atom abstraction. The following four step plan was devised:

A. Determine the global rate constant for reaction of the primary fluoroalkyl radical, **1**, with sodium 4-(1-propenyl)-benzoate ($CH_3CH{=}CHC_6H_4CO_2Na$, **2**) in water by lfp.

B. Use **2** as a kinetic "probe" to determine the rate constants for H-abstraction by **1** from THF and isopropanol.

C. Determine the rate constant for deuterium abstraction from THF-d_8 by **1** *via* a direct competition between H-atom abstraction from THF and deuterium atom abstraction from THF-d_8.

D. Determine the relative rate constants for H-atom abstraction from a series of organic substrates *vs.* D-atom abstraction from THF-d_8 *via* competition experiments and then convert these to absolute rate constants.

A lfp measurement of the rate constant for addition of 1 to 2

Radical **1** was generated "instantaneously" by 308 nm lfp of the parent iodide, **3**, in water at ambient temperature. In the presence of **2** an absorption grows in at 320 nm. This grow-in follows pseudo-first-order kinetics and the "global" rate constant can be calculated from the experimental growth curves measured over a range of concentrations of **2** (eqn. 1).

$$k_{\mathrm{exptl}}\,(320\ \mathrm{nm}) = k_o + k_{gl}[\mathbf{2}] \qquad (1)$$

As discussed earlier,[15] the global reactions of **1** with an alkene such as **2** are comprised almost entirely of addition, with less than 5% being due to H-atom abstraction, *i.e.*, $k_{gl} \approx k_{\mathrm{add}}$. The slope of the plot of k_{exptl} values *vs.* [**2**] yields the second order rate constant, $k_{\mathrm{add}} = 3.9_5 \times 10^7\ \mathrm{M^{-1}s^{-1}}$.

B lfp "probe" experiments

Although the alkyl radicals derived by H-atom abstraction from THF and isopropanol have insufficient extinction coefficients to be monitored by UV-vis spectroscopy, the rate constants for the reactions of these H-donors with **1** can be obtained by using **2** as a kinetic "probe",[21] see eqn. 2.

$$k_{\mathrm{exptl}}\,(320\ \mathrm{nm}) = k_o + k_{gl}[\mathbf{2}] + k_{\mathrm{H}}[\text{H-Donor}] \qquad (2)$$

The experimental pseudo-first-order rate constant is now the sum of the rate constants for addition to **2** and H-atom abstraction from the H-donor. At constant [**2**] eqn. 3 holds and:

$$k_{\mathrm{exptl}}\,(320\ \mathrm{nm}) = k_o' + k_{\mathrm{H}}[\text{H-Donor}] \qquad (3)$$

Plots of k_{exptl} *vs.* [H-Donor] gave straight line fits with R^2 greater than 0.96 in all cases. The second order rate constants, k_{H}, for H-atom abstraction are readily calculated from the slopes of these lines. For THF and isopropanol, $k_{\mathrm{H}} \approx 3.3 \times 10^4$ and $4.0 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$, respectively (each an average of three or more individual experiments). It should be noted that the lfp probe method provides the most accurate rate constants when both probe and substrate react with fairly high rate constants ($\geq 10^6$–$10^7\ \mathrm{M^{-1}\ s^{-1}}$). Because both THF and isopropanol have low rate constants (roughly three orders of magnitude smaller than that for the probe), they had to be employed at high concentrations (up to 3 M) and the probe at low concentrations (1.7 mM). Under these conditions, the derived rate constants for H-atom abstraction from THF and isopropanol are much less reliable than is "normal" in such experiments and we suggest the errors are likely to be about ± 30%. (See electronic supplementary information (ESI) for tables of kinetic data. †)

C Competition experiment to determine k_D for THF-d_8

The reaction of the perfluoroiodide, **3**, with THF using UV initiation proceeds *via* a clean, rapid free radical chain process to give reduced product, $\mathbf{4}_{\mathrm{H}}$, in essentially quantitative yield.

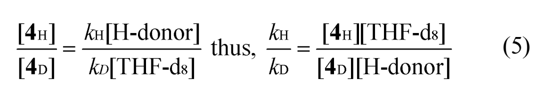
$$\underset{\mathbf{3}(\mathrm{NaO_3SR_fI})}{\mathrm{NaO_3SCF_2CF_2OCF_2CF_2I}} \;\underset{\sim\ \text{quant.}}{\xrightarrow[\mathrm{THF,\ H_2O}]{h\nu,\ \mathrm{RT}}}\; \underset{\mathbf{4}(\mathbf{NaO}_3\mathrm{SR_fH})}{\mathrm{NaO_3SCF_2CF_2OCF_2CF_2H}}$$

The ratio of the rate constant for H-atom abstraction from THF to D-atom abstraction from THF-d_8, was determined by using various mixtures of THF and THF-d_8 and measuring $[NaO_3SR_fH]/[NaO_3SR_fD]$ ratios. As reported earlier,[9] the ^{19}F NMR signals for $\boldsymbol{H}CF_2CF_2OCF_2CF_2SO_3^-$ ($\mathbf{4}_{\mathrm{H}}$) and $\boldsymbol{D}CF_2CF_2OCF_2CF_2SO_3^-$ ($\mathbf{4}_{\mathrm{D}}$) are well-separated (by 0.7 ppm) and a simple integration of the signals provides the relative concentrations of these two products. A plot of the $[\mathbf{4}_{\mathrm{H}}]/[\mathbf{4}_{\mathrm{D}}]$ ratios *vs.* the [THF]/[THF-d_8] ratios gives a straight line (see eqn. 4), the slope of which yields the kinetic isotope effect, $k_{\mathrm{H}}/k_{\mathrm{D}} = 7.9 \pm 0.4$ and hence $k_{\mathrm{D}} = 3.3 \times 10^4/7.9 = 4.2 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$.

$$\frac{[\mathbf{4}_{\mathrm{H}}]}{[\mathbf{4}_{\mathrm{D}}]} = \frac{k_{\mathrm{H}}[\mathrm{THF}]}{k_{\mathrm{H}}[\text{THF-}d_8]} \qquad (4)$$

D Obtaining relative and absolute H-atom abstraction rate constants from other substrates

Competition experiments using THF-d_8 and an H-donor permitted fast, clean, high yield reactions with virtually all of the organic substrates studied, as depicted below.



$$\mathrm{IR_fSO_3Na}\ (\mathbf{3}) + \text{H-Donor vs THF-}d_8 \xrightarrow{h\nu,\ \mathrm{H_2O}} \mathrm{HR_fSO_3Na}\ (\mathbf{4}_{\mathrm{H}}) + \mathrm{DR_fSO_3Na}\ (\mathbf{4}_{\mathrm{D}})$$

$$\frac{[\mathbf{4}_{\mathrm{H}}]}{[\mathbf{4}_{\mathrm{D}}]} = \frac{k_{\mathrm{H}}[\text{H-donor}]}{k_D[\text{THF-}d_8]} \ \text{thus,}\ \frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{[\mathbf{4}_{\mathrm{H}}][\text{THF-}d_8]}{[\mathbf{4}_{\mathrm{D}}][\text{H-donor}]} \qquad (5)$$

The relative rate constants, $k_{\mathrm{H}}/k_{\mathrm{D}}$, are obtained by plotting the ratio of substrate concentrations *versus* product ratios. A typical plot of $[\mathbf{4}_{\mathrm{H}}]/[\mathbf{4}_{\mathrm{D}}]$ *vs.* [H-Donor]/[THF-d_8] is shown for isopropanol in Fig. 2. Values of $k_{\mathrm{H}}/k_{\mathrm{D}}$ and the values of k_{H} derived therefrom are collected in Table 1.

Table 1 Rate constants for H-atom abstraction from various H-donors by $^{-}O_3SCF_2CF_2OCF_2CF_2^{\bullet}$ (**1**) in water at 25 °C, relative to D-atom abstraction from THF-d_8, absolute rate constants and, for comparison, absolute rate constants for H-atom abstraction by n-$C_4F_9^{\bullet}$ in 1,3-bis(trifluoromethyl)benzene (BTB) at the same temperature

H-donor	k_H/k_D[a] **1** in H_2O	10^3 k_H/M^{-1} s^{-1}[b] **1** in H_2O	10^3k_H/M^{-1} s^{-1}[c] n-$C_4F_9^{\bullet}$ in BTB[9]
CH_3OH	0.43	1.8	0.92
CH_3CH_2OH	2.8	12	3.0[d]
$(CH_3)_2CHOH$	11.4	48[e]	16
$(CH_2OH)_2$	1.28	5.4	—
$(CH_3CHOH)_2$	5.6	24	5.0
$CH_3CO_2CH_2OH$	0.59	2.5	—
CF_3CH_2OH	0.019	0.08	—
$(CF_3)_2CHOH$	0.094	0.39	—
THF	7.9	33[f]	31
$(CH_3OCH_2)_2$	1.3	5.5	6.7
CH_3COCH_3	0.015	0.06	—
CH_3CO_2H	0.005	0.02	—
$CH_3CH_2CO_2H$	0.18	0.76	—
$CH_3CO_2^{-}Na^{+}$	0.028	0.12	—
$CH_3CH_2CO_2^{-}Na^{+}$	0.36	1.5	—
$HSCH_2CH_2SO_3^{-}Na^{+}$	96	400	—
$(HOCH_2CH_2CH_2)_3SiH$	28	120	—
$Br^{-}Me_3N^{+}CH_2SiMe_2H$	20.5	86	—
H_3PO_3	3.5	15	—

[a] SD generally ~ 5–10%, for full details see ESI.† [b] Based on $k_D = 4.2 \times 10^3$ M^{-1} s^{-1}, see text. [c] From reference 7. [d] This work. [e] Lfp gave $k_H = 40 \times 10^3$ M^{-1} s^{-1}, see text. [f] Value determined by lfp probe experiment and upon which all other rate constants are based.

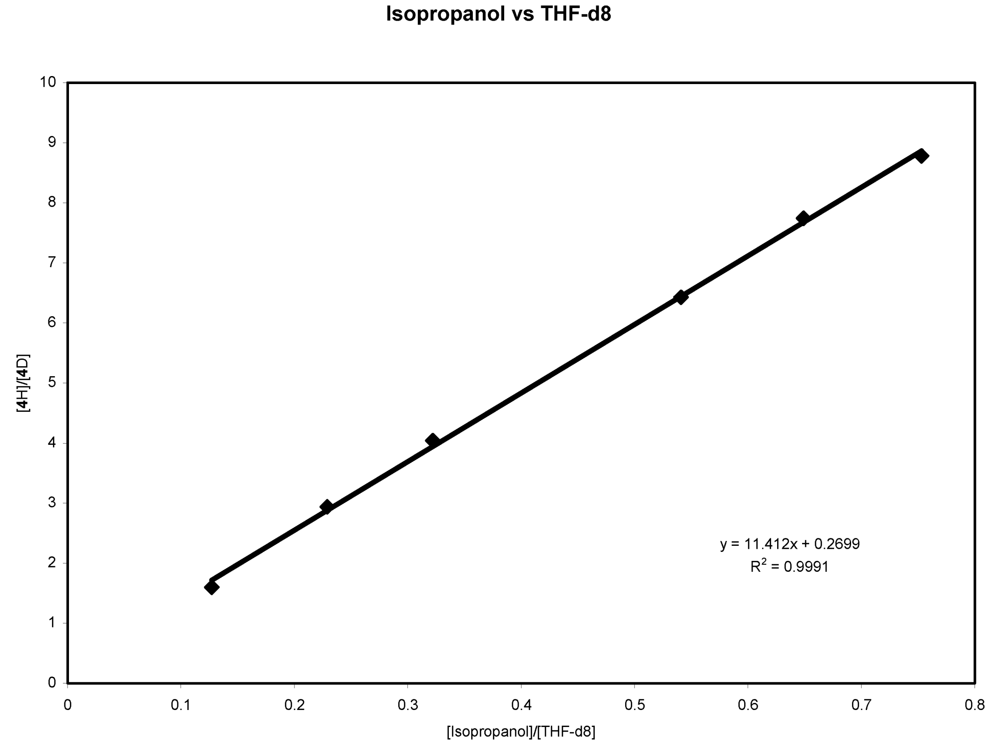


Fig. 2 Plot of [4_H]/[4_D] *vs.* [isopropanol]/[THF-d_8] $k_H/k_{D(THF\text{-}d8)}$ = slope = 11.4 (±0.2).

Discussion

Before considering the k_H rate constants given in Table 1 it is necessary to establish that the k_H/k_D ratios are not influenced by: (i) the small (0.5%) protic impurity in the (99.5%) THF-d_8, nor (ii) proton transfer from the water solvent to radical **1**. With regard to (i), since k_H/k_D = 7.9 for THF/THF-d_8 (*vide supra*, section C) plots of $\mathbf{4}_H/\mathbf{4}_D$ *vs.* [H-donor]/[THF-d_8] are expected to have a positive intercept, which will partially derive from the H-content in the THF-d_8. In a control reaction with THF-d_8 alone, an intercept of 7.9 × 0.5% = 0.04 was expected due simply to the H-content of the THF-d_8. This was confirmed when a $\mathbf{4}_H/\mathbf{4}_D$ ratio of 0.04–0.05 was observed. Thus, non-zero intercepts do not compromise the accuracy of the slopes of these plots, from which k_H/k_Dvalues are derived. They derive from a combination of experimental error and the small H-content in THF-d_8.

With regard to (ii), one can at least imagine that some $\mathbf{4}_D$ might be replaced by $\mathbf{4}_H$ *via* an electron transfer from THF-d_8 to **1**, yielding the **1** anion which would be very rapidly protonated to yield a $\mathbf{4}_H/\mathbf{4}_D$ ratio which did not reflect H- and D-atom abstraction rates, *i.e.*:

$$\text{THF-d}_8 + \mathbf{8} \xrightarrow{H_2O} (\text{THF-d}_8)^{+\bullet} + \mathbf{1}^{-}$$
$$\mathbf{1}^{-} + H^{+} \rightarrow \mathbf{4}_H$$

These reactions can be ruled out by the results described above for THF-d_8 alone in water. They were more firmly ruled out by showing that no $\mathbf{4}_D$ was produced in a reaction carried out with THF in D_2O.

Rate constants for H-atom abstractions in water by primary fluoroalkyl radicals

Rate constants for the eight alcohols show the expected response to structural factors in terms both of C–H bond dissociation enthalpies (BDEs) and inductive effects. Thus, the increase in k_H along the series CH_3OH < CH_3CH_2OH < $(CH_3)_2CHOH$ (Table 1) can be primarily attributed to a decrease in the α-C–H BDEs along the series (*viz.*,[22] 94, 93 and 91 kcal mol^{-1}, respectively). Comparison of the rate constants for methanol, ethanol and isopropanol (1.8, 12 and 48 × 10^3 M^{-1} s^{-1}, respectively, Table 1) with those reported for reaction of the CF_3 radical with the same alcohols in water, *viz.*,[23] 8, 46 and 92 × 10^3 M^{-1} s^{-1}, respectively, indicates that primary fluoroalkyl radicals are somewhat less reactive than trifluoromethyl in H-atom abstractions, a reactivity difference we have previously reported for their additions to C=C double bonds.[13] Rates of H-atom abstraction from the β-CH position in alcohols are reduced by inductive electron withdrawing (EW) neighboring atoms or groups because EW disfavors the polar effects which can stabilize the transition state and, hence, enhance the reactivity of a substrate (see Fig. 1). Thus, $(CH_2OH)_2$ and $(CH_3CHOH)_2$ are only half as reactive, respectively, as CH_3CH_2OH and $(CH_3)_2CHOH$, despite having twice as many α-CH hydrogen atoms. Even larger rate retarding polar effects are seen in the two fluoroalcohols which are only 0.7–0.8% as reactive as their non-fluorinated counterparts (Table 1). Rate constants for H-atom abstraction from carbon are also small for compounds containing EW carbonyl, ester and carboxylic acid groups some of which are so unreactive that they might be suitable as solvents for chain reactions involving fluorinated radicals. The carboxylate anions are more reactive than the corresponding carboxylic acids. This result further suggests that polar effects play a role in stabilizing/destabilizing the transition state. That is, any rate reduction due to Coulombic repulsion between the negative charges on the carboxylate anion and the radical's sulfonate group is more than compensated for by the inductive electron donating ability of the CO_2^- group (F = −0.10 *vs.* F = +0.34 for CO_2H).[24]

As would be expected, H-atom abstractions from ethers occur at rates comparable to the rates of abstraction from alcohols. THF is six times as reactive towards **1** as $(CH_3OCH_2)_2$. A six-fold difference at −60 °C[25] (dropping to a two-fold difference at 27 °C)[26] has previously been reported for the rates of H-atom abstraction from THF and $(CH_3CH_2)_2O$ by *tert*-butoxyl radicals. The higher reactivity of THF was attributed to favorable stereoelectronic (anomeric) factors in which conjugative electron delocalization stabilizes the oxyalkyl radical reaction product and thereby decreases the C–H BDE in THF relative to diethyl ether because of the small dihedral angle between the oxygen's lone pair(s) of electrons and the α-C–H bonds in THF.

The water-soluble thiol and two water-soluble silanes are sufficiently reactive towards **1** that they might prove useful as chain transfer agents in fluoroalkyl radical chain reactions.

Comparison of rate constants for H-atom abstraction by primary fluoroalkyl radicals in water and in BTB

The four alcohols for which the comparison is possible have k_H values 2–5 times greater in water than in BTB but the two ethers show no significant solvent effect on their k_H values. We have previously reported that primary fluoroalkyl radicals add to the C=C double bonds of styrenes *ca.* 5–9 times and to 1-alkenes *ca.* 3 times more rapidly in water[14] than in F113.[15] It was concluded[14] that these modest rate enhancements derived, at least in part, from stabilization of the polar transition state for addition of the electrophilic fluorinated radical to alkenes by the polar solvent, water. This is reasonable because the C=C double bond in an alkene, and even more so that in a styrene, is readily polarized and the developing negative and positive charges in the transition state (Fig. 3) are well separated and, hence, can be solvated by water molecules. This is not the case for a H-atom abstraction where any charge separation occurs over a much shorter distance and the transition state is more reminiscent of an intimate ion pair (see Fig. 1) than a solvent separated ion pair (see Fig. 3).

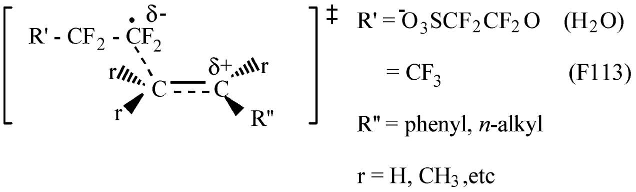


Fig. 3 Polar transition state for addition to a C=C double bond.

The absence of significant solvent effects on H-atom abstraction from hydrocarbons by *tert*-butoxyl radicals was first proposed by Walling and coworkers in the early 1960's[27–29] who observed that *tert*-butanol/acetone product ratios, which reflect competition between H-atom abstraction and β-scission of the *tert*-butoxyl radical, showed large solvent effects. It was argued that: "Solvent interaction with the transition state for β-scission presents no difficulties, but in the transition state involving an alkoxy(l) radical and a substrate such as cyclohexene, solvent molecules should be sterically excluded from close vicinity to the alkoxy(l) radical."[27] Accordingly, the large solvent effects on *tert*-butanol/acetone ratios were ascribed "to solvation of the transition state for the β-scission process."[29] This analysis was proven correct some 30 years later when direct, time-resolved, lfp kinetic measurements showed that there was no kinetic solvent effect on H-atom abstraction from cyclohexane by *tert*-alkoxyl radicals.[30]

The absence of a kinetic solvent effect on H-atom abstractions from hydrocarbons by *tert*-butoxyl radicals and its explanation provides a rationale for the essential identity of the rate constants for H-atom abstraction from the two ethers by primary fluoroalkyl radicals in water and BTB (see Table 1). An alternative, but more complex, explanation would be that for the ethers there are two effects of water, one rate enhancing and one rate retarding, which are, fortuitously, exactly in balance. Rate enhancement would be due to stabilization of the polar transition state by water (Fig. 1). Rate retardation could arise from the formation of hydrogen bonds between water and the lone pairs of electrons on the ether's oxygen atom which would impair the ability of these lone pairs to stabilize the developing radical center in the transition state by conjugative electron delocalization. However, Occam's razor does not favor this more complex explanation of observed facts.

This leaves the problem of the modest (2–5 fold) rate enhancements in water *vs.* BTB for H-atom abstraction from the alcohols (Table 1). We tentatively suggest that this is due to hydrogen bond formation between the hydroxyl group of the alcohol and a water molecule (Fig. 4). This will increase the electron density on the oxygen atom of the alcohol and enhance the ability of the lone pairs on this atom to stabilize the developing radical center by conjugative electron delocalization.

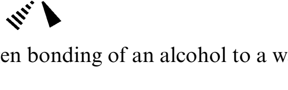


Fig. 4 Hydrogen bonding of an alcohol to a water molecule.

Conclusions

We have previously shown that the rates of addition of fluorinated primary alkyl radicals to C=C double bonds are larger by a factor of 3–9 in water than in a solvent of low polarity.[14] We have now discovered that the rates of H-atom abstraction by these radicals from alcohols are only 2–5 times faster in water than in a low polarity solvent. Moreover, H-atom abstraction from ethers is unaffected by solvent polarity, a result congruent with earlier work on H-atom abstraction from hydrocarbons by *tert*-alkoxyl radicals.[27–30] The disappointing conclusion is that the reactivities of these very electron-deficient carbon-centered radicals can, at best, be modulated to only a minor extent by changes in the solvent.

Experimental

Kinetic measurements by time-resolved laser flash photolysis

The apparatus and procedures have been described in detail elsewhere.[14,31] The radicals, $^{\bullet}R_fSO_3^-$ (**1**), were generated "instantaneously" by 308 nm lfp of aqueous solution of the parent iodide (**3**) at ambient temperature.

Verification of probe addition rate constant

The rate constant for addition, k_{add} (k_{gl}), to the spectroscopic probe, $CH_3CH{=}CHC_6H_4CO_2Na$ (**2**), was obtained (duplicate runs) in the usual manner to give values of $(3.9 \pm 0.5) \times 10^7$ and $(4.0 \pm 1.0) \times 10^7\ M^{-1}\ s^{-1}$, mean $3.9_5 \times 10^7\ M^{-1}\ s^{-1}$, *cf.* $(3.3 \pm 0.3) \times 10^7\ M^{-1}\ s^{-1}$ measured previously.[14] In any set of experiments, the probe's concentration was kept constant (see ESI †) and the grow-in of the absorption at 320 nm was monitored.

Laser flash photolysis probe experiments

The procedure has been described in detail previously.[15,21] 1.5 mL of aqueous solutions (0.027 M) of IR_fSO_3Na, **3**, in quartz cuvettes (8 × 8 mm) sealed with rubber septa were deaerated by flushing with N_2 for 20 minutes, then the various amounts (50–400 µL) of deaerated THF or isopropanol and the volume of the sample was made up (when necessary) to 2.0 mL. After addition of 100 µL of a stock solution (32.9 to 35.7 mM) of **2**, the mixture was vortexed for 20 seconds and purged with nitrogen for a further 2–5 minutes. The growths of the optical density at 320 nm following each of 6 to 9 pulses of a 308 nm laser were recorded for each concentration of H-atom donor. These growth traces of the radical were analyzed by least-squares fitting on the basis of pseudo-first-order kinetics to obtain experimental rate constants, k_{exp} (320 nm). As described in the Results, the experimental rate constant is the sum of the rate constants for all competitive processes.[21]

Sodium 5-*H*-3-oxaoctafluoropentanesulfonate (4_H)

$ICF_2CF_2OCF_2CF_2SO_3Na{\cdot}H_2O$[9] (0.28 g, 0.60 mmol) was dissolved in 45 ml THF. The solution was degassed by bubbling with nitrogen for 30 minutes. After the solution had been UV irradiated for 24 hours, ^{19}F NMR analysis showed complete consumption of the starting material. The THF was removed on a rotary evaporator and the solid residue was washed with hexanes, then with diethyl ether, and dried under reduced pressure to give the title compound in 88% yield: mp 132 °C, dec.; ^1H NMR (acetone-d_6), δ 6.48 (tt, 1H, J_1 = 3.4 Hz, J_2 = 52 Hz); ^{19}F NMR (acetone-d_6), δ −81.6 (m, 2F), −88.7 (br s, 2F), −117.6 (br s, 2F), −138.2 (dt, 2F, J_1 = 4.3 Hz, J_2 = 51 Hz); HRMS (FAB), (M + Na): calcd 342.9263; found 342.9256. Analysis for $C_4F_8HNaO_4S{\cdot}H_2O$: calcd C 14.21, H 0.89; found C 14.20, H 0.61%.

(Dimethylsilyl)methyltrimethyl ammonium bromide

(Bromomethyl)dimethylsilane[32] (1.38 g, 9.0 mmol) was dissolved in 25 mL CH_3CN in a 3-neck round bottom flask equipped with a magnetic stir bar and a gas inlet. Trimethylamine was bubbled into the solution, and a white precipitate was formed. The solid was filtered, washed with diethyl ether, and dried under reduced pressure. ^1H NMR showed a peak at 3.20 ppm, and its integral was much more than that of other peaks. The compound was used in its H-abstraction kinetic study without further purification: ^1H NMR (D_2O/H_2O), δ 4.21 (br s, 1H), 3.20 (s), 0.28 (d, 6H, J = 3.6 Hz); ^{13}C NMR (D_2O): δ 56.75, 55.6, −5.1.

Hydrogen atom donors

All the compounds listed in Table 1 were available commercially except for the two silanes.

Tris(3-hydroxypropyl)silane

Tris(3-benzyloxypropyl)silane[33,34] (0.64 g, 1.4 mmol) was dissolved in 40 mL ethanol in a 3-neck round bottom flask equipped with a magnetic stir bar, a gas inlet connected with hydrogen cylinder, and a rubber septum. The system was flushed with N_2, charged with 10% Pd/C (0.26 g, 0.08 mmol), and then filled with H_2. The absorption of H_2 was very obvious as soon as stirring started. After 3 h of stirring at room temperature, the resulting suspension was filtered through Celite. The filtrate was evaporated and the residue was solidified with diethyl ether to afford the silane as a white solid in 97% yield, mp 89–91 °C. ^1H NMR (D_2O/H_2O): δ 3.54 (t, 6H, J = 6.6 Hz), 1.57 (m, 6H), 0.60 (m, 6H). ^{13}C NMR (CD_3OD/CH_3OH) 66.0, 27.6, 12.45. HRMS (FAB): calcd for $C_9H_{21}SiO_3$ (M − 1) 205.1260, found 205.1252.

General procedure for kinetic studies

The kinetic studies were run in pyrex NMR tubes containing a sealed capillary tube ($CFCl_3$ in C_6D_6) as the internal standard. For each kinetic study, a group of samples were prepared at the same time. The NMR tubes were capped with rubber septa, and wrapped with Teflon tape before chemicals were added. The IR_fSO_3Na was used as a stock solution (17.8% by weight) and added to the NMR tubes with a micro-syringe. All liquid chemicals were added with syringes and weighed on a balance. The samples were degassed by three freeze-pump-thaw cycles. After ^{19}F NMR spectra were taken, the samples were irradiated using a RPR-204 Rayonet photochemical reactor. The ^{19}F NMR spectrum was taken again after 24 hours. The NMR acquisition time was at least 15 minutes to assure accurate integration. The product ratios were obtained from the ratios of integration of the CF_2H and CF_2D signals. The conversion and yield were obtained from the integration of the CF_2I peak in the starting material and the (CF_2H + CF_2D) peaks in the products relative to the internal standard.

Tables and plots of kinetic data are available in the ESI. †

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