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Rate constants for hydrogen abstraction from alkoxides by a perfluoroalkyl radical. An oxyanion accelerated process†

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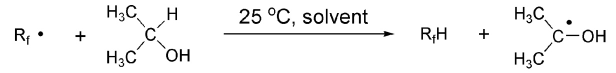
A combination of laser flash photolysis and competitive kinetic methods has been used to measure the absolute bimolecular rate constants for hydrogen atom abstraction in water from a series of fluorinated alkoxides and aldehyde hydrates by the perfluoroalkyl radical, $^{\bullet}CF_2CF_2OCF_2CF_2SO_3^-\ Na^+$. The bimolecular rate constants observed for the β-fluorinated alkoxides were in the $10^5\ M^{-1}\ s^{-1}$ range, such rates representing enhancements (relative to the respective alcohols) of between 100 and almost 1000-fold, depending on the reactivity of the alkoxide. Likewise, the monobasic sodium salts of chloral and fluoral hydrate exhibit similar rate enhancements, relative to their respective hydrates.

Introduction

Soon after the discovery by Evans of the huge rate accelerations exhibited during anionic oxy-Cope rearrangements,[1,2] it was hypothesized that such accelerations were related to *the bond-weakening effect* of the anionic alkoxy group on the adjacent C_3–C_4 bond.[3] The basic conclusions derived from Goddard's GVB theory work have recently been confirmed and elaborated upon by Houk[4] and Baumann[5] using DFT methodology. Houk, for example, found that the C–H BDE of methoxide ion was ~23 kcal less than that of methanol.[4] Such weakening of the α-C–H bonds of alkoxides should provide acceleration to other reactions that involve the breaking of such bonds, and such has been found to be the case,[6] examples being alkoxy-accelerated [1.3]-sigmatropic rearrangements,[7–10] the Ireland Claisen rearrangement of allyl ester enolates,[11,12] and even 1,5-hydrogen or alkyl shifts.[13,14]

In recent years we have been successful in developing reliable competition methods for determining the absolute rate constants for abstraction of hydrogen from organic substrates by perfluorinated radicals.[15–17] As exemplified below, isopropanol is fairly reactive towards perfluoroalkyl radicals in both the non-polar solvent 1,3-bis-trifluoromethylbenzene (BTB) and in water, with this hydrogen abstraction reaction being modestly faster in water than in BTB.



Rf •	Solvent	k_H
$CF_3CF_2CF_2CF_2$ •	BTB	$1.6\ (0.3) \times 10^4 M^{-1}s^{-1}$
$Na^+\ ^-O_3SCF_2CF_2OCF_2CF_2$ •	H_2O	$4.8\ (1.6) \times 10^4 M^{-1}s^{-1}$

Although electrostatic and polar effects can have a dramatic effect on the C–H abstraction rates from organic compounds by a fluorinated radical, when working with a series of similar compounds, the relative rates of H-abstraction by $Na^{+-}O_3$-$CF_2CF_2OCF_2CF_2^{\bullet}$ correlate well with their relative C–H BDE's, as shown for the series of alcohols in water below.[16,17] The bond dissociation energies of methanol, ethanol, and isopropanol in Table 1 were estimated by first optimizing the geometries of the alcohols and their corresponding α-hydroxy radicals at the B3LYP/6-31G(d) level and then calculating their single point energies at the B3LYP/6-311+G(2df,2p) level.

Table 1 Correlation of C–H homolytic reactivity with alcohol bond dissociation energies

Alcohol	k_H(per H)/ $10^4\ M^{-1}\ s^{-1}$	k_{rel}	BDE's (calcd)/ kcal mol^{-1}
CH_3OH	0.6 (0.2)	(1)	93
CH_3CH_2OH	6 (2)	10	91
$(CH_3)_2CHOH$	48 (16)	80	89

We considered it an intriguing prospect to probe the quantitative impact of the bond-weakening effects of an alkoxide substituent on the rate constants of hydrogen abstraction reactions. To our knowledge, the only related previous work is that of Bunnett in which he found that methoxide ion was a good hydrogen atom donor to aryl radicals,[18,19] methoxide, for example, being about 45 times better than methanol in donating a hydrogen atom to the *p*-nitrophenyl radical.[20]

In order for us to carry out a kinetic study of hydrogen abstraction from alkoxides, it would, of course, be necessary for the alkoxide substrate to be present in the competition mixture as a totally homogeneous solute, something that would be impossible in both the BTB and the aqueous medium, the latter because the basicities of the alkoxides would preclude their existence in water. However, as a part of our kinetic studies on H-atom abstraction by fluorinated radicals from alcohols in water, we have also determined the rate constants for H-abstraction from trifluoroethanol and hexafluoroisopropanol. Because of the polar and electrostatic influence of the fluorine substituents, these two compounds were, predictably, orders of magnitude less reactive than their hydrocarbon counterparts, as seen in Table 2.[16,17]

However, these alcohols have one property that that was extremely propitious in view of our interest in the kinetics of H-atom abstraction from alkoxides – *they are much more acidic*

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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/b4/b405074f

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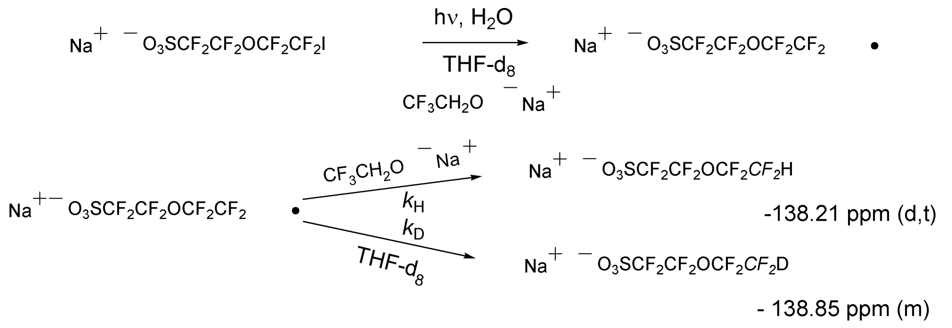


Table 2 Contrast of rate constants for hydrogen abstraction from fluorinated and nonfluorinated alcohols

Alcohol	$k_H/10^3$ M^{-1} s^{-1}	k_{rel}
CH_3CH_2OH	12 (4)	
CF_3CH_2OH	0.08 (0.02)	150
$(CH_3)_2CHOH$	48 (16)	
$(CF_3)_2CHOH$	0.39 (0.12)	123

than their fluorine-free counterparts, having pK_a's of 12.4 and 9.3, respectively.[21] Their conjugate bases, the alkoxides, would therefore be relatively weak, stable and homogeneously soluble in water.

Results and discussion

Relative rate constants for H-atom abstraction by $Na^{+-}O_3CF_2CF_2OCF_2CF_2^{\bullet}$ from sodium trifluoroethoxide (TFEO), sodium hexafluoroisopropoxide (HFIPO), and sodium trifluoroisopropoxide, $(CF_3)(CH_3)CHO^-Na^+$ (TFIPO),[22] were first determined by competition kinetics involving H-transfer from the alkoxide *versus* D-transfer from perdeuterio tetrahydrofuran, THF-d_8. The general procedure has been described. These relative rate constants were converted to absolute values using the rate constant, $k_D = 4.2 \times 10^3$ M^{-1} s^{-1}, previously determined by combining a laser flash photolysis (LFP) direct measurement of the rate constant for H-atom abstraction from non-deuterated THF with competition experiments involving THF and THF-d_8, all in water. The results obtained (see Table 3 below) demonstrate that all three alkoxides are not only very much more reactive than their respective parent alcohols, but that they are also considerably more reactive than the corresponding non-fluorinated alcohols. This high reactivity undoubtedly derives from a combination of the bond-weakening effect of the alkoxide function and the enhanced nucleophilicity of the alkoxide C–H bond towards the highly electrophilic perfluoro radical.

LFP measurements of the rate constants for H-atom abstraction by $Na^{+-}O_3CF_2CF_2OCF_2CF_2^{\bullet}$ from TFEO and HFIPO met with mixed success. For TFEO the LFP value for k_H was 11×10^4 M^{-1} s^{-1}, which is in reasonable agreement with the 7.7×10^4 M^{-1} s^{-1} obtained by competition, as described above, particularly when it is remembered that the estimated reliability of these LFP-derived rate constants is *ca.* ±30% and that the competitive method for obtaining absolute rate constants relies, ultimately, on an LFP measurement.[16] However for HFIPO the observed LFP k_H was 50×10^4 M^{-1} s^{-1}, which is 4.5 times greater than the competition value of 11×10^4 M^{-1} s^{-1}. It seemed probable that this large difference was due to some unidentified problem[23] in the LFP experiment because the competition experiment conformed to our strict standards with respect to conversion, yield, lack of side products, *etc.* Nevertheless, additional competition experiments designed to validate the competition method in this system were carried out as described below.

First a *direct kinetic competition between the two alkoxides* using sodium 2-*deuterio*hexafluoroisopropoxide in competition with sodium 2,2,2-trifluoroethoxide (TFEO), with *no* THF being involved. Combining this measured k_H/k_D value (4.64) with the value of the primary isotope effect ($k_H/k_D = 5.88$) for H- *vs.* D-abstraction from HFIPO,[24] and using the rate constant of 7.7×10^4 M^{-1} s^{-1} for TFEO, yields a rate constant (k_H) for HFIPO of 9.8×10^4 M^{-1} s^{-1}.

Table 3 Rate constants for hydrogen abstraction from alkoxides and alcohols

Alkoxide/Alcohol Hydrogen Donor	$k_H/10^3$ M^{-1} s^{-1}	k_{rel}
$CF_3CH_2O^-Na^+$ (TFEO)	77 (20)	
CF_3CH_2OH	0.08 (0.02)	962
$(CF_3)_2CHO^-Na^+$ (HFIPO)	108 (30)	
$(CF_3)_2CHOH$	0.39 (0.12)	277
$(CF_3)(CH_3)CHO^-Na^+$ (TFIPO)	155 (50)	
$(CF_3)(CH_3)CHOH$	1.5 (0.5)	100

Secondly, a "reverse" competition experiment was carried out, using *deuterated* HFIPO $[(CF_3)_2CDO^-Na^+]$ and undeuterated THF. This gave a k_H/k_D value of 1.94, which when combined with the k_H value for THF (3.3×10^4 M^{-1} s^{-1}) and the HFIPO isotope effect ($k_H/k_D = 5.88$) provides a value for k_H of HFIPO of 10×10^4 M^{-1} s^{-1}. There is therefore a self consistency in the values of k_H for HFIPO that were obtained from the three different competition studies (11, 9.8 and 10×10^4 M^{-1} s^{-1}), and we feel confident that their average, *viz.* 10.8×10^4 M^{-1} s^{-1}, can be regarded as a reliable value for the k_H of HFIPO.

Aldehyde hydrates and their monosodium salts are also of interest and relevant to the present work because they can be regarded as α-hydroxy-substituted alcohols and alkoxides. Again, in order to study such compounds in water, one must have aldehyde hydrates that (a) exist virtually 100% in the hydrate form when in water, and (b) are acidic enough that their monobasic forms are stable in water. Chloral and fluoral hydrate meet these requirements nicely, the presence of the three β-chlorines or fluorines insuring that the hydrates are exclusively present in water, and that they are sufficiently acidic to cleanly form their monosodium salts upon treatment with one equivalent of NaH. In fact the pK_a's of chloral and fluoral hydrate have been estimated to be 10.1 and 10.2, respectively.[25] Because of the inductive effect of the three β-halogens, these hydrates, like the fluorinated alcohols, should be poor H-atom donors to $Na^{+-}O_3CF_2CF_2OCF_2CF_2^{\bullet}$. This is borne out by the data in Table 4, which shows that chloral hydrate is slightly more reactive than fluoral hydrate, which is slightly more reactive than trifluoroethanol, results which are consistent with stabilization of the carbon-centered radicals formed from the hydrates by the "extra" α-hydroxy group. More significantly, the monosodium salt of fluoral hydrate exhibits the largest enhancement, relative to its non-alkoxy counterpart (k_{rel} = 1315), as well as the largest rate constant that we have yet observed for H transfer from carbon to the fluorinated radical, $Na^{+-}O_3CF_2CF_2OCF_2CF_2^{\bullet}$: $k_H = 1.7 \times 10^5$ M^{-1} s^{-1}.

Conclusions

In conclusion, an alkoxide functionality has long been known to provide marked acceleration to sigmatropic processes wherein a bond to the carbon bearing the alkoxy group is

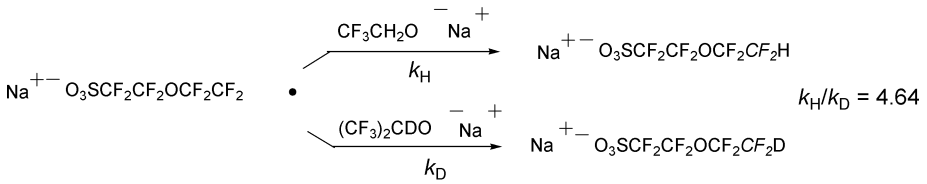
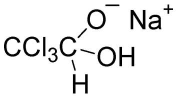
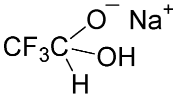


Table 4 Rate constants of hydrates and hydrate monoanions

Hydrate/hydrate monoanion	$k_H/10^3$ M^{-1} s^{-1}	k_{rel}
$CCl_3CH(OH)_2$	0.83 (0.25)	
	157 (50)	189
$CF_3CH(OH)_2$	0.13 (0.04)	
	171 (50)	1315
CF_3CH_2OH	0.08 (0.02)	

broken. Absolute rate data now demonstrate that an α-alkoxide also dramatically enhances homolytic hydrogen atom abstractions, in particular, by highly electrophilic perfluoro radicals. Thus, β-fluorinated alkoxides exhibit bimolecular rate constants for H-abstraction by a fluorinated radical in the 10^5 M^{-1} s^{-1} range, such rates representing enhancements (relative to the respective alcohols) of between 100 and almost 1000-fold, depending on the reactivity of the alkoxide. Likewise, the monobasic sodium salts of chloral and fluoral hydrate exhibit similar rate enhancements, relative to their respective hydrates.

Experimental

All reagents used were commercially available, and were purchased from CIL, Aldrich, Fisher, or Lancaster. 1,1,1-Trifluoroacetaldehyde hydrate was purchased from SynQuest Laboratories. All reagents were used without further purification.

NMR spectra and kinetic ^{19}F NMR measurements were performed at 282 MHz using a Varian VXR-300 spectrometer. All chemical shifts reported are in ppm downfield from the internal standard, $CFCl_3$.

Typical procedure for preparation of alkoxide sodium salts. Hexafluoroisopropoxide, sodium salt

NaH (0.534 g, 22 × 10^{-3} mol) was suspended in 30 cm^3 of diethyl ether. The suspension was stirred and cooled to ice bath temperature. Hexafluoroisopropanol (3.1 g, 31 × 10^{-3} mol) was added to 15 cm^3 of diethyl ether and then added dropwise *via* an addition funnel to the NaH suspension. The solution was allowed to stir for 3 hours during which time it reached room temperature. The ether was removed by rotovap and the resulting solid dried *via* vacuum pump overnight to obtain hexafluoroisopropoxide, sodium salt (2.66 g, 98.2% yield): ^1H NMR (300 MHz, D_2O) δ 4.42 (hept, J_{HF} = 6.9 Hz, 1H); ^{19}F NMR (282 MHz, D_2O) δ −76.58 (d, J_{FH} = 6.5 Hz, 6H).

Typical procedure for the preparation of monobasic sodium salts of hydrates. Chloral hydrate, sodium salt

NaH (0.290 g, 12 mmol) was suspended in 30 cm^3 of diethyl ether. The suspension was stirred and cooled to ice bath temperature at which time chloral hydrate (2.0 g, 12 mmol) in 15 cm^3 of diethyl ether was added dropwise. The solution was allowed to stir for 3 hours, reaching room temperature. The ether was then removed by rotovap and the resulting solid dried *via* vacuum pump overnight to obtain chloral hydrate, sodium salt (2.20 g, 97% yield): ^1H NMR (300 MHz, D_2O) δ 4.19 (s, 1H). For fluoral hydrate sodium salt, ^1H NMR (D_2O) δ 5.28 (q, 1H). ^{19}F NMR (D_2O) δ −85.58 (d, 3F).

General procedure for ^{19}F kinetic experiments

The kinetic experiments were run in NMR tubes containing a sealed capillary tube of C_6D_6 and $CFCl_3$ as the internal standard. The NMR tubes were capped with natural rubber septa, and sealed with Teflon tape before any chemicals were added. Using a micro-syringe, 15 μL (6.04 × 10^{-6} moles) of IR_fSO_3Na solution were added to each tube. Exact amounts of stock salt solutions were added to each NMR tube using micro-syringes. Equal amounts of THF-d_8 were added to each tube, along with varying amounts of the hydrogen donor. Deionized water was added to each NMR tube so that the total volume of reaction mixture was 565 μL. The samples were degassed 3 times using the freeze–pump–thaw method. Subsequent to the initial ^{19}F NMR spectra taken, the samples were irradiated for 16 hours in the RPR-204 Rayonet photochemical reactor. ^{19}F NMR spectra were again taken, and all peaks of significance were integrated. The product ratios were obtained from the integration of the CF_2H (d, –138.3 ppm) and CF_2D (s, −139.0 ppm) peaks. The conversion and yield were obtained by integration of the $CFCl_3$ peak in the starting material and the integration of the product peaks.

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

Kinetic measurements by time-resolved laser flash photolysis. The apparatus and procedures have been described in detail elsewhere.[26,27] The radicals, $^{\bullet}CF_2CF_2OCF_2CF_2SO_3$ Na, were generated "instantaneously" by 308 nm LFP of aqueous solution of the precursor iodide[16] at ambient temperature. Since the products of the $^{\bullet}CF_2CF_2OCF_2CF_2SO_3$ Na reaction with H atom donors, TFEO, HFIPO, and TFIPO were not easily observed, the rate constants of the process, k_{gl}, were obtained by measurements of the rate of adduct formation of $^{\bullet}CF_2CF_2OCF_2CF_2SO_3$ Na with 1.7 ± 0.4 mM sodium 4-(1-propenyl)benzoate ($CH_3CH{=}CHC_6H_4CO_2Na$) as a spectroscopic probe monitored at 320 nm.

Probe addition rate constant. The rate constant for addition, k_{add} (k_{gl}), to the spectroscopic probe, $CH_3CH{=}CHC_6H_4CO_2Na$, was taken to be $3.9_5 \times 10^7$ M^{-1} s^{-1}.[16] In any set of experiments, the probe's concentration was kept constant 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.[28,29] 1.5 cm^3 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 during 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 cm^3. 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

Table 5 Experimental LFP rate constants

Hydrogen Donor	$k_{gl}/10^4$ M^{-1} s^{-1}
CF_3CH_2ONa	11.3 ± 0.1
CF_3CH_2ONa	10.0 ± 0.1
$(CF_3)_2HCONa$	49.2 ± 2.8
$(CF_3)_2HCONa$	51.5 ± 3.4

constants, $k_{exp(320nm)}$. The experimental rate constant is the sum of the rate constants for all competitive processes.[29]

Preparation of samples for laser flash photolysis. The procedure of the "probe method" was described in detail previously.[29] 1.5 cm^3 of aqueous solutions (0.027 M) of IR_f-SO_3Na in quartz cuvettes (8 × 8 mm) sealed with rubber septa were deaerated by flushing with N_2 during 20 minutes, then the various amounts (50–300 μL) of deaerated aqueous solution of H-atom donors were added with microliter syringe, and the mixtures were vortexed during 20 seconds. The measurements of the growth of the optical density at 320 nm during 6 to 9 pulses of 308 nm laser were recorded for each concentration of H-atom donor. The transient growth traces of the radical were analyzed by least-squares fitting, on the basis of pseudo-first-order kinetics, to obtain experimental rate constants, $k_{exp(320nm)}$.

Kinetics measurements using the "spectroscopic probe method". The observed experimental rate constant is a sum of the rate constants of competitive processes:

$$k_{exp(320\ nm)} = k_o + k_{probe}[probe] + k_{gl}\,[\mathit{H\text{-}donor}]$$

thus, if [probe] = *constant*, the $k_{exp(320\ nm)} = k' + k_{gl}\,[\mathit{H\text{-}donor}]$. Indeed, values of ($k_{exp(320\ nm)} - k_{probe}[probe]$) plotted *vs.* [*H-donor*] gave straight line fits with R^2 greater than 0.96 in almost all cases (see ESI†) and the absolute second order rate constants k_{gl} for $^{\bullet}R_fSO_3^-$ reaction with the H-atom donors were obtained. The rate constants k_{gl} for the alkoxide donors in aqueous solutions are listed in Table 5.

Computational

The geometries of methanol, propanol, isopropanol, and their corresponding α-hydroxy radicals were optimized at the B3LYP/6-31G(d) level. Single point energies were then calculated at the B3LYP/6-311+G(2df,2p) level. The restricted B3LYP was used for closed-shell systems and the unrestricted method for open shell systems. All the calculations were performed by using the Gaussian-03 suite of programs.[30] An accepted value from experiment for the C–H dissociation is D_{298} = 94 ± 2 kcal mol^{-1} and calculations (QCISD(T)/G-311G+G(3df,2p)//MP2/6-31G*) by the late John Pople predicted D_{298} = 96.2 kcal mol^{-1}.[31]

Acknowledgements

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References and notes

1 D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.*, 1975, **97**, 4765.
2 D. A. Evans, D. J. Baillargeon and J. V. Nelson, *J. Am. Chem. Soc.*, 1978, **100**, 2242.
3 M. L. Steigerwald and W. A. Goddard III, *J. Am. Chem. Soc.*, 1979, **101**, 1997.
4 H. Y. Yoo, K. N. Houk, J. K. Lee and M. A. Scialdone, *J. Am. Chem. Soc.*, 1998, **120**, 205.
5 H. Baumann and P. Chen, *Helv. Chim. Acta*, 2001, **84**, 124.
6 S. R. Wilson, *Org. React.*, 1993, **43**, 93.
7 T. Cohen, M. Bhupathy and J. R. Matz, *J. Am. Chem. Soc.*, 1983, **105**, 520.
8 R. L. Danheiser, C. Martinez-Davila and H. Sard, *Tetrahedron*, 1981, **37**, 3943.
9 S.-H. Kim, S. Y. Cho and J. K. Cha, *Tetrahedron Lett.*, 2001, **42**, 8769.
10 N. J. Harris and J. J. Gajewski, *J. Am. Chem. Soc.*, 1994, **116**, 6121.
11 R. E. Ireland, P. Wipf and J. D. Armstrong III, *J. Org. Chem.*, 1991, **56**, 650.
12 F. E. Ziegler, *Chem. Rev.*, 1988, **88**, 1423.
13 L. A. Paquette, G. D. Crouse and A. K. Sharma, *J. Am. Chem. Soc.*, 1980, **102**, 3972.
14 P. J. Battye and D. W. Jones, *Chem. Commun.*, 1984, 990.
15 A. B. Shtarev, F. Tian, W. R. Dolbier Jr. and B. E. Smart, *J. Am. Chem. Soc.*, 1999, **121**, 7335.
16 L. Zhang, J. Cradlebaugh, G. Litwinienko, B. E. Smart, K. U. Ingold and W. R. Dolbier Jr., *Org. Biomol. Chem.*, 2004, **2**, 689.
17 L. Zhang, The Addition and Hydrogen Abstraction Reactions of a Fluorinated Radical in Aqueous Solution, Ph. D. Dissertation, University of Florida, Gainesville, 2001.
18 J. F. Bunnett, *Acc. Chem. Res.*, 1992, **25**, 2.
19 See also: S. E. Vaillard, A. Postigo and R. A. Rossi, *J. Org. Chem.*, 2004, **69**, 2037.
20 W. J. Boyle Jr. and J. F. Bunnett, *J. Am. Chem. Soc.*, 1974, **96**, 1418.
21 C. M. Timperley and W. E. White, *J. Fluorine Chem.*, 2003, **123**, 65.
22 There is some uncertainty about the pK_a of trifluoroisopropanol, but one would expect it to be slightly less acidic than trifluoroethanol.[21]
23 Both H-bonding and, particularly, ion pairing (with the metal counterion) are known to cause large variations in alkoxide-accelerated rate constants.[10] Indeed kinetic studies on alkoxide-accelerated sigmatropic processes[10] have shown that anything that influences the degree of free charge on the alkoxide will significantly influence the degree of acceleration provided by the alkoxide.
24 J. Cradlebaugh, L. Zhang, A. B. Shtarev, B. E. Smart and W. R. Dolbier Jr., *Org. Biomol. Chem.*, 2004, DOI: 10.1039/b405075d (following paper).
25 J. L. Kurz and M. A. Stein, *J. Phys. Chem.*, 1976, **80**, 154.
26 L. Zhang, W. R. Dolbier Jr., B. Sheeller and K. U. Ingold, *J. Am. Chem. Soc.*, 2002, **124**, 6362.
27 S. Kazanis, A. Azarani and L. J. Johnston, *J. Phys. Chem.*, 1991, **95**, 4430.
28 D. V. Avila, K. U. Ingold, J. Lusztyk, W. R. Dolbier Jr., H. Q. Pan and M. Muir, *J. Am. Chem. Soc.*, 1994, **116**, 99.
29 H. Paul, R. D. Small Jr. and J. C. Scaiano, *J. Am. Chem. Soc.*, 1978, **100**, 4520.
30 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh PA, 2003.
31 L. A. Curtiss, L. D. Kock and J. A. Pople, *J. Chem. Phys.*, 1991, **95**, 4040.