was added dropwise. After 16 h the reaction was quenched with acetic acid. Evaporation under reduced pressure provided a residue that was taken up in CH_2Cl_2 and washed with water. Chromatography (3 × 30) with petroleum ether removed the hydrocarbons. Subsequent elution with CH_2Cl_2 yielded 1.52 g (92%) **19**: mp 202–203 °C; IR (KBr) 3395 (NH), 1641 (amide I), 1510 cm^{-1} (amide II); ^1H NMR δ 1.74 (m_c, 3 CH_2 of adamantyl far from position 1), 1.87 (m_c, 3 CH_2 of adamantyl next to position 1), 2.06 (m_c, s-like, 3 CH of adamantyl), 2.17 (d, J = 19.1 Hz, 10-H pseudo ax), 2.45 (dd, J = 14.0 Hz, J = 7.8 Hz, 1 H of benzylic CH_2), 2.81 (dd, J = 14.0 Hz, J = 4.1 Hz, 1 H of benzylic CH_2), 3.16 (dd, J = 10.5 Hz, J ca 2.5 Hz, NCCH), 3.23 (d, J = 19.0 Hz, 10-H pseudo eq), 4.46 (d, J = 2.3 Hz, 9-H pseudo eq), 4.58–4.75 (m, NCH), 5.52 (d, J = 9.0 Hz, NH), 6.33 (m_c, d-like, 2 ortho H of nonbenzylic Ph), 6.90–7.03 (m, 6 Ar H), 7.11–7.30 (m, 9 Ar H), 7.49 (m_c, d-like, 1 Ar H). Anal. Calcd for $C_{40}H_{41}NO$: C, 87.07; H, 7.49; N, 2.54. Found: C, 87.09; H, 7.53; N, 2.27.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemie. This support is gratefully acknowledged. We thank Professor Hans Suschitzky for his help in improving the English.

Registry No. **1a**, 7646-66-4; **2a**, 98943-73-8; **3a**, 70686-42-9; **4a**, 614-17-5; **8**, 50688-77-2; **9**, 98943-92-1; **10**, 16180-99-7; **11**, 92367-87-8; **18**, 119297-89-1; **19**, 119297-90-4; AH_2, 120-12-7; XH, 92-83-1.

The Philicity of *tert*-Butoxy Radicals. What Factors Are Important in Determining the Rate and Regiospecificity of *tert*-Butoxy Radical Addition to Olefins?

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The relative rates of addition of *tert*-butoxy radicals to substituted styrenes have been evaluated by means of competition experiments. The data demonstrate that *tert*-butoxy radicals show electrophilic character (ρ = −0.30). An explanation for the apparently anomalous behavior shown by *tert*–butoxy radicals in their reactions with fluoro olefins is proposed in terms of the ability of α-fluorine substituents to stabilize the incipient C–O bond.

Tedder's "rules"[1] for radical addition reactions indicate that, while regiospecificity is controlled mainly by steric factors, the rate of radical addition to the unsubstituted terminus of 1-substituted or 1,1-disubstituted olefins is determined largely by polar factors. This is in accordance with the finding that trends in the reactivities of radicals toward monomers can often be rationalized in terms of the nucleophilic (e.g. methyl,[1] *n*-hexyl, cyclohexyl, *tert*-butyl[2,3]) or electrophilic (e.g. trifluoromethyl,[1] hydroxy,[4] benzoyloxy[5]) character of the attacking radical.

tert-Butoxy radical reactions have been widely studied.[6] Most work has been devoted to hydrogen atom abstraction, for which *tert*-butoxy radicals have a marked propensity. Studies on the rates of abstraction of benzylic hydrogens from substituted toluenes and subsequent analysis of the data by way of a Hammett correlation indicate that *tert*-butoxy radicals are slightly electrophilic (small negative ρ, see Table I).[7-11] Zavitsas and Pinto,[9] and later, Levin and Abul'khanov,[12] disputed that tert-butoxy radicals have any marked electrophilic character. They suggested that the correlation with Hammett σ was fortuitous and proposed that changes in the C–H bond dissociation

Table I. ρ and ρ^+ Parameters for Reactions of Oxygen- and Carbon-Centered Radicals

	addition to styrene		abstraction from toluene	
radical	ρ^+	ρ	ρ^+	ρ
$(CH_3)_3C^{\bullet}$	1.1,*a*			0.49[b]
$c\text{-}C_6H_{11}^{\bullet}$	0.68[a]			
$n\text{-}C_6H_{13}^{\bullet}$	0.45[a]			
$n\text{-}C_{11}H_{23}^{\bullet}$				0.45[c]
$CH_3^{\bullet}$			−0.1[e]	−0.12 (−0.21)[d,e]
$CCl_3^{\bullet}$	−0.42[f]	−0.43[f]	−1.46[g]	−1.46 (−1.67)[d,g]
$(CH_3)_3CO^{\bullet}$	−0.27[h]	−0.31[i]	−0.35[j]	−0.34 (−0.36)[d,j]
$(CH_3)_3COO^{\bullet}$			−0.56[k]	−0.78 (−0.76)[d,k]

[a] 42 °C, ρ increases with decreasing temperature.[2] [b] 80 °C, Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885–2891. See also: Dutsch, H. R.; Fischer, H. *Int. J. Chem. Kinet.* **1982**, *14*, 195–200. Pryor, W. A.; Davis, W. H.; Staneley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4754–4756. [c] 80 °C, Henderson, R. W.; Ward, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 7556–7557. See also: Pryor, W. A.; Davis, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 7557–7559. Zavitsas, A. A.; Hanna, G. M. *J. Org. Chem.* **1975**, *40*, 3785–3783. [d] Values in parentheses are those recalculated by Pryor et al.[30] with data for meta-substituted toluenes only. [e] 100 °C, Pryor, W. A.; Tonellato, U.; Fuller, D. L.; Jumonville, S. *J. Org. Chem.* **1969**, *34*, 2018–2020. [f] 70 °C, meta-substituted styrenes only.[36] [g] 50 °C, Huyser, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 394–396. [h] 60 °C, present work see Figure 2. [i] 60 °C, present work, meta-substituted styrenes only, see Figure 1. [j] 45 °C, chlorobenzene (value of ρ shows a small solvent dependence).[7] [k] 30 °C, Howard, J. A.; Chenier, J. H. B. *J. Am. Chem. Soc.* **1973**, *95*, 3054–3055.

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(9) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390–7396.

(10) Cheun, Y. G.; Hwang, M. S.; Lee, I. *Taehan Hwahakoe Chi* **1983**, *27*, 391–398; *Chem. Abstr.* **1984**, *100*, 85186*w*.

(11) For a summary of earlier studies on the reactions of t-butoxy radicals with substituted toluenes see ref 9.

(12) Levin, Ya. A.; Abul'khanov, A. G. *Zh. Org. Chem.* (*Engl. Transl.*) **1980**, *16*, 414–427.

Scheme I

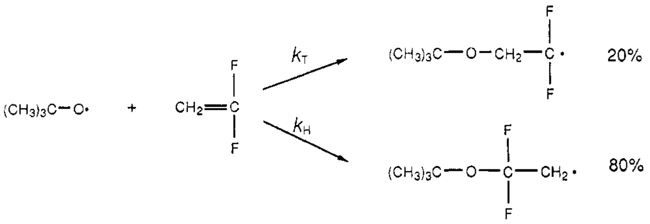

Table II. Relative Rates and Regiospecificities for Addition of Radicals to Halo Olefins[1,22]

	$(CH_3)_3CO^\bullet$ (60 °C)		$CH_3^\bullet$ (164 °C)		$CF_3^\bullet$ (164 °C)	
	k(rel)[a]	k_H/k_T[b]	k(rel)[a]	k_H/k_T[b]	k(rel)[a]	k_H/k_T[b]
$CH_2{=}CH_2$	1.0		1.0		1.0	
$CH_2{=}CHCl$	2.0	0.017		<0.01		<0.01
$CH_2{=}CHF$	0.7	0.36	1.1	0.2	0.5	0.1
$CH_2{=}CF_2$	1.1	4.0		1	0.2	0.04
$CHF{=}CF_2$	6.7	4.5	5.8	2.1	0.05	0.5

[a] Overall rate constant relative to that for reaction with ethylene. In accordance with normal practice, the rate constant for additon to ethylene has been reduced by a factor of two to allow for the two equivalent sites of attack. [b] The rate constant for tail addition (k_T) is that for addition to the end of the double bond with most hydrogens (cf. Scheme I).

energies are the principle cause for the rate variations observed in hydrogen atom abstraction. This view was in turn questioned. A large body of work now exists to show that many factors, including bond dissociation energies, influence the rate of hydrogen atom abstraction[1] and clearly demonstrate that polar factors play an important role.[1,13,14]

Bertrand and Surzur observed for a series of oxygen-centered radicals (of which *tert*-butoxy was the most nucleophilic) that the abstraction:addition ratio increases with increasing nucleophilicity of the attacking radical.[15] Houk has rationalized the high propensity for abstraction vs addition in terms of the relative nucleophilicity of *tert*-butoxy radicals.[16]

There have been several studies on the factors that govern the rate of addition of *tert*-butoxy radicals to carbon–carbon double bonds.[6,17–22] The influences of remote alkyl substitution on the rate of addition to simple alkenes[17] or α,β-unsaturated esters[18] can be rationalized in terms of the electrophilicity of *tert*-butoxy radicals. Sato and Otsu[19] determined the relative rates for attack of *tert*-butoxy radicals on a series of monomers and compared these with literature data for methyl, phenyl, and benzoyloxy radicals. They concluded that *tert*-butoxy radicals have electrophilic character but rationalized a different order of monomer reactivities for benzoyloxy and *tert*-butoxy by suggesting that resonance effects were also important in determining reactivity.

Scheme II

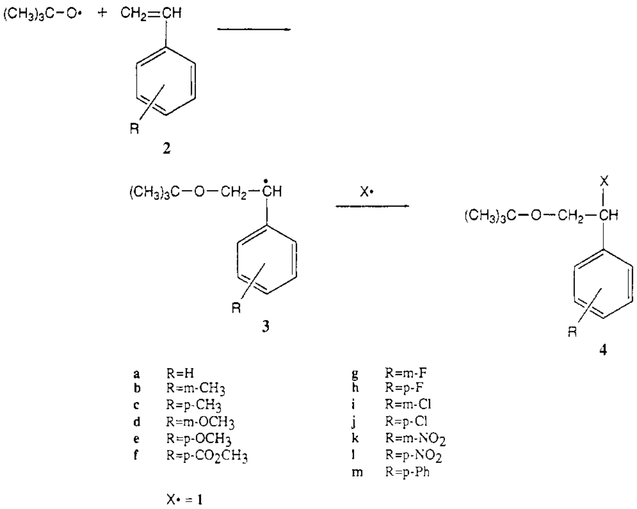

Table III. Relative Reactivity (k/k_s) of Substituted Styrenes toward *tert*-Butoxy Radicals

styrene, R =	k/k_s[a]	styrene, R =	k/k_s[a]
2a, H	1.0	**2g**, *m*-F	0.807 ± 0.004 (10)
2b, *m*-CH_3	1.087 ± 0.005 (8)	**2b**, *p*-F	1.012 ± 0.006 (6)
2c, *p*-CH_3	1.305 ± 0.004 (4)	**2i**, *m*-Cl	0.782 ± 0.008 (5)
2d, *m*-OCH_3	1.012 ± 0.005 (11)	**2j**, *p*-Cl	1.113 ± 0.016 (2)
2e, *p*-OCH_3	1.932 ± 0.012 (4)	**2k**, *m*-NO_2	0.627 ± 0.004 (4)
2f, *p*-CO_2CH_3	0.740 ± 0.008 (4)	**2l**, *p*-NO_2	0.881 ± 0.038 (5)
		2m, *p*-Ph	1.312 ± 0.007 (4)

[a] The quoted errors are the standard deviation from mean. The number of determinations is given in parentheses. $k_s \sim 10^6\ M^{-1}\ s^{-1}$ (cf. Bednarek, D.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1988**, *21*, 1522–1528).

In 1974, Kochi found that *tert*-butoxy addition to vinylidene fluoride affords predominantly "head" addition (refer Scheme I).[21] This result was surprising, since consideration of steric factors (admittedly small), polar factors (assuming electrophilic *tert*-butoxy), or the influence of fluorine substitution on radical stability leads to the expectation that tail addition should be favored. A more extensive study of the reactions of *tert*-butoxy radicals with a series of halo olefins has recently been carried out in these laboratories.[22] The results confirmed Kochi's finding for vinylidene fluoride and showed, for the fluoro olefins, a trend in reactivities more typical of a nucleophilic species (see Table II).

Ionization potentials and SOMO energies have been proposed as a rough measure of radical electrophilicity (a lower ionization potential or SOMO energy indicates greater electrophilicity.[23,24] It is, therefore, noteworthy that while the ionization potential for *tert*-butoxy radical

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(13) For further discussion on the role of polar factors in radical abstraction reactions see ref 1 and references cited in the footnote to Table I.

(14) Other recent studies attesting to the polar character of *tert*-butoxy radicals include: Mahiou, B.; Gleicher, G. J. *J. Org. Chem.* **1987**, *52*, 1555–1559. Kim, S. S.; Koo, H. M.; Choi, S. Y. *Tetrahedron Lett.* **1985**, *26*, 891–894. Kim, S. S.; Sohn, S. C. *Tetrahedron Lett.* **1982**, *23*, 3703–3706. Davies, A. G.; Quintard, J. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1163–1167.

(15) Bertrand, M. P.; Surzer, J.-M. *Tetrahedron Lett.* **1976**, 3451–3454.

(16) Houk, K. W. In *Frontiers of Free Radical Chemistry*; Pryor, W. A., Ed.; Academic Press: New York, 1980; pp 60–71.

(17) Cuthbertson, M. J.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1957–1973.

(18) Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1573–1588.

(19) Sato, T.; Otsu, T. *Makromol. Chem.* **1977**, *178*, 1941–1950.

(20) Korth, H.-G.; Sustmann, R. *Tetrahedron Lett.* **1985**, *26*, 2551–2554. Griffiths, P. G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1982**, *23*, 1309–1312. Gilbert, B. C.; Marshall, P. D. R.; Norman, R. O. C.; Pineda, N.; Williams, P. S. *J. Chem. Soc., Perkin Trans. 2* 1981, 1392–1399. Encina, M. V.; Rivera, M.; Lissi, E. A. *J. Polym. Chem. Ed.* **1978**, *16*, 1709–1717.

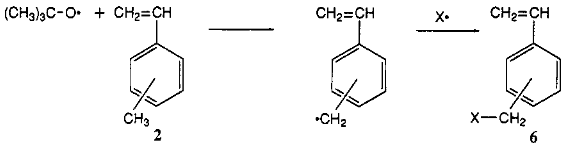
(21) Elson, I. H.; Mao, S. W.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 335–342.

(22) Cuthbertson, M. J.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1985**, *38*, 315–324.

(23) Flemming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976; p 176.

(24) Elliot, R. J.; Richards, W. G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 943–945.

Scheme III

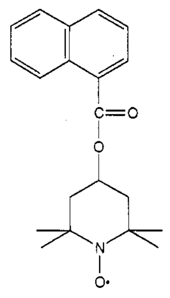


(IP = −12 eV) is low with respect to methyl radical (IP = −9.8 eV),[23] MO calculations suggest that the energies of the SOMO's of these two radicals are very similar.[24] In the recent literature, methyl radical is generally considered a nucleophilic radical[1] (see, however, Table I).

In order to clarify which factors govern the rate of addition of *tert*-butoxy radicals to olefins we have examined the relative rates of addition of *tert*-butoxy radicals to a series of substituted styrenes (Scheme II).[25]

Results and Discussion

The relative rates (k/k_s, where k_s is the rate constant for reaction with styrene) were determined by means of competition experiments employing the trapping technique described in previous work.[17,26] This involved decomposing di-*tert*-butyl peroxalate (the source of *tert*-butoxy radicals) in a solution of the nitroxide (**1**)[27] and styrene(s)



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(**2a–m**) in benzene. Low (10%) concentrations of styrene(s) were used so as to keep the reaction medium as constant as possible. It is well known that the polarity of the reaction medium can have a substantial effect on *tert*-butoxy radical reactivity.[6,28] The nitroxide concentration (0.05 M) was chosen such that methyl radicals and the radicals (**3a–m**) were efficiently scavenged. For each data point (Table III) at least two competition experiments were conducted, each with a different selection of **2a-m**. As a further control, a set of competition experiments was carried out, each using the same selection of styrenes and initiator concentration but with different initial nitroxide concentrations (0.05, 0.1, 0.2 M). The distribution of the styrene-derived alkoxyamines (**4a–m**) showed no dependence on the nitroxide concentration.

The reactivities of **2a–m** could also be determined in single monomer experiments utilizing β-scission of *tert*-butoxy radicals to methyl radicals and acetone as a clock reaction[29] [i.e. based on the yield of alkoxyamines (**4a–m**) relative to that of the methoxyamine (**5**)]. It was found that values of k/k_s determined in this way agreed with those obtained in the competition experiments to within ±2%.

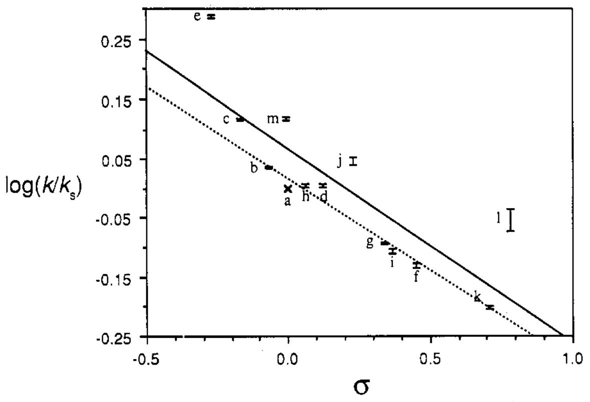


Figure 1. Correlation of log (k/k_s) for styrenes **2a–m** (see Table III) with Hammett σ parameter. The solid line is the result of a least-squares fit to all points [log (k/k_s) = 0.066 − 0.329σ, r = 0.74]. The dashed line is the result of a least-squares fit for the meta-substituted styrenes only [log (k/k_s) = 0.016 − 0.309σ, r = 0.98].

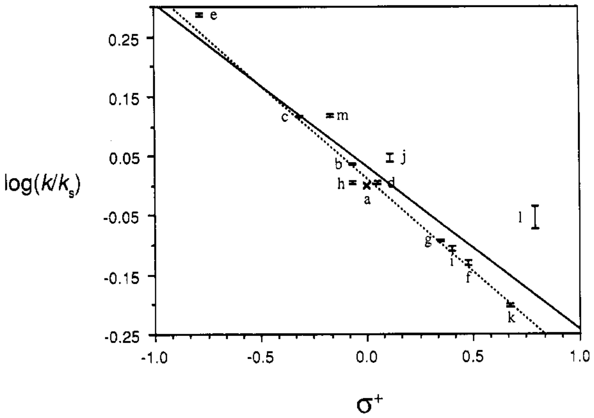
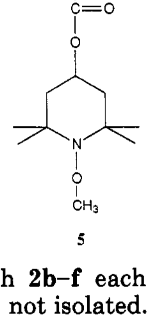


Figure 2. Correlation of log (k/k_s) for styrenes **2a–m** (see Table III) with σ^+. The solid line is the result of a least-squares fit to all points [log (k/k_s) = 0.032 − 0.273σ^+]. A better correlation may be obtained by omission of the p-NO$_2$ point [log (k/k_s) = 0.025 − 0.330σ^+, r = 0.96]. The dashed line is the result of a least-squares fit for the meta-substituted styrenes only [log (k/k_s) = 0.013 − 0.313σ^+, r = 0.99].



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The reactions with **2b–f** each gave one additional product. These were not isolated. They are tentatively ascribed to the alkoxyamines (**6**, see Scheme III) that arise by trapping the radical formed by abstraction of a hy-

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[25] A preliminary account of this work has been published. See: Solomon, D. H.; Moad, G. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 109–125.

[26] Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1979**, *1*, 529–534.

[27] Nitroxide (**1**) was chosen as scavenger because of the high extinction of the 1-naphthoyl chromophore at 300 nm where the phenylethyl group has negligible or zero absorbance thus simplifying quantitative HPLC. The alkoxyamines (**4a–e** and **4g–j**) have identical extinctions at this wavelength (ϵ_{300} = 5970 ± 20) and HPLC response ratios. The relative responses of **4f,k–m** were, however, not equal and so were determined by a comparison of HPLC and NMR integrations of mixtures with ethyl naphthoate.

[28] The relative reactivity of *tert*-butoxy radicals toward vinyl monomers has been shown to be dependent on the polarity of the reaction medium. See: Grant, R. D.; Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 2447–2454. Grant, R. D.; Rizzardo, E.; Solomon, D. H. *Makromol. Chem.* **1984**, *185*, 1809–1817.

[29] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

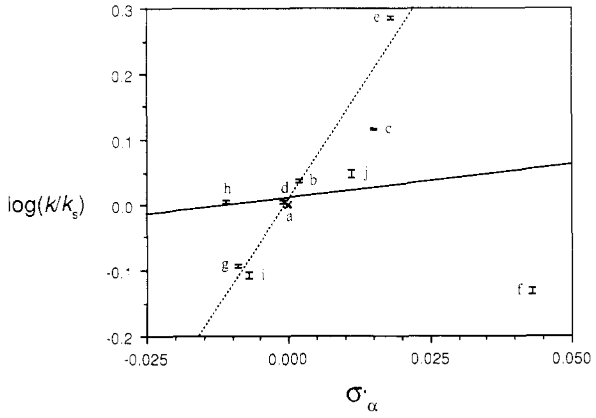

Figure 3. Correlation of log (k/k_s) for styrenes **2a–j** (see Table III) with $\sigma^{\bullet}_{\alpha}$. The solid line is the result of a least-squares fit to all points [log $(k/k_s) = 0.010 + 0.985\sigma^{\bullet}_{\alpha}$, $r = 0.017$]. The dashed line is the result of a least-squares fit for the meta-substituted styrenes only [log $(k/k_s) = 0.075 + 13.1\,\sigma^{\bullet}_{\alpha}$, $r = 0.94$]. There are no $\sigma^{\bullet}_{\alpha}$ values for *m*- or *p*-NO_2 or *p*-Ph substituents.

drogen from the methyl groups of **2b–f**.

Hammett Correlation. Arguments for the use of σ,[30] σ^+, $\sigma^{\bullet}$,[31-33] or other parameters in establishing linear free energy relationships for reactions involving radicals have appeared in recent literature. The values of log (k/k_s) (Table III) are correlated with Hammett σ in Figure 1 and Brown σ^+ in Figure 2.[34,35] It is generally found that the use of σ^+ gives a substantially better correlation for radical reactions. The present system is no exception.

An appreciably better correlation with σ is obtained by considering only the meta-substituted styrenes. Any para substituent may stabilize the product radical by resonance, and it has been suggested that the departure from a straight line correlation of log (k/k_s) for para-substituted styrenes with σ should be taken as a measure of the importance of product radical stability in determining reaction rates.[30] In this context, it is notable that the para-substituted derivatives have reactivities greater than or equal to those expected on the basis of the correlation with the meta-substituted styrenes (i.e. the points lie above the lines drawn in Figure 1). A similar finding was made by Sakurai et al.[36] in their study of the reactions of trichloromethyl radicals with substituted styrenes. Indeed, it is noteworthy that the relative reactivities established in this work correlate well with those of the electrophilic trichloromethyl radical {log $(k/k_s)_{tBuO\bullet} = 0.666[\log (k/k_s)_{CCl_3\bullet}]$; $r = 0.97$}.

Arnold's $\sigma^{\bullet}_{\alpha}$ parameters[32] are based on the hyperfine coupling constants for the α-hydrogens of substituted benzylic radicals. These are stated to be a direct measure of the influence of the substituent on the degree of spin delocalization and hence of the stabilities of the benzylic radicals. A poor correlation is found between $\sigma^{\bullet}_{\alpha}$ and log (k/k_s) (Figure 3). Equally poor correlations are found with Creary's $\sigma^{\bullet}_{c}$[33] or Jackson's $\sigma^{\bullet}$[31] parameters. This finding is consistent with the reaction having an essentially reactant-like transition state with little localization of the free spin at the incipient radical center and is in line with the prevailing view, as recently expressed by Tedder[1] and Giese,[37] that product radical stability typically plays only a minor role in determining radical reactivity in additions to olefins.

However, consistent with the view that deviation of log (k/k_s) values for the para-substituted styrenes from a straight-line correlation with σ or σ^+ is due to stabilization of the incipient radical center, a dual parameter approach, employing σ or σ^+ and either of the $\sigma^{\bullet}$ parameters mentioned above, provides acceptable correlations. For example, log $(k/k_s) = 0.057 + 1.257\,\sigma^{\bullet}_{\alpha} - 0.456\sigma$, $r = 0.91$.[38]

In Table I, our present results are compared with data for addition of some other carbon- and oxygen-centered radicals to substituted styrenes and with corresponding data for abstraction from substituted toluenes. In both processes the product is a substituted benzyl radical. Comparison of the ρ or ρ^+ values for *tert*-butoxy radical addition and abstraction suggests that the two processes have similar sensitivity to polar factors. For both reactions the ρ or ρ^+ parameters for *tert*-butoxy radicals are negative and are significantly less than those for simple alkyl radicals. It is clear that *tert*-butoxy radicals exhibit electrophilic character in their addition to styrene derivatives.

Comment on Factors Affecting the Regiospecificity of Addition to the Fluoro Olefins. There has been much discussion on the reactions of radicals with fluoro olefins and the factors that control regiospecificity. A detailed study of these and other reactions led Tedder[1] to propose a set of rules by which the outcome of radical addition might be qualitatively predicted.

The differences in regiospecificity shown by methyl and various fluoromethyl radicals in their reactions with the fluoro olefins (see Table II) were ascribed, by and large, to polar influences.[1] It was proposed that methyl radicals give predominantly head addition with 1,1,2-trifluoroethylene and show low specificity in their reactions with the other fluoro olefins because their relative nucleophilicity favors attack at the more electron-poor (the more fluorine substituted) end of the double bond.

The pattern reactivities shown by *tert*-butoxy radical parallels more closely that of methyl radical rather than a more electrophilic species (see Table II). This finding led to the electrophilicity of *tert*-butoxy radicals being questioned (see the introduction).[22] The present data confirm that *tert*-butoxy radicals have electrophilic character. This necessitates an alternative explanation (other than inherent nucleophilicity) for the behavior of *tert*-butoxy radicals in their reactions with the fluoro olefins (see the introduction).

Tedder[1,39] has pointed out that the nature of the incipient bond is of paramount importance in determining the rate and regiospecificity of radical addition reactions. We should therefore anticipate that just as factors that hinder formation of this bond (e.g. bulky substituents at the point

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of attack) retard addition, factors that stabilize the new bond should facilitate addition.

We propose that the anomalous behavior of *tert*-butoxy radicals with the fluoro olefins may be associated with the relative strengths of the bonds being formed in head vs tail addition (e.g. CF_2–O vs CH_2–O for 1,1-difluoroethylene). While there is little experimental data on specific models that would enable the influence of this effect to be quantified, it is noteworthy that the C–O bond dissociation energies in CF_3–O–CF_3 and CF_3–OH are greater by 22 and 18 kcal mol^{-1} respectively than those in CH_3–O–CH_3 and CH_3–OH.[40] If only a fraction of this is reflected in the transition state we can readily account for the observed regiospecificity.

Support for this hypothesis comes from the recent studies of Arnaud et al.[41] and Canadell et al.[42] who have independently carried out theoretical studies on the reactions of methyl radicals with the fluoro olefins. One of the main points to emerge from these studies is that the strength of the incipient bond is extremely important in determining the rate of addition. Their calculations show that the stabilization afforded a C–C bond by the α-fluorine substituents is an important factor in determining the regiospecificity of addition. They also show that addition to the more fluorinated end of the double bond is the more thermodynamically favored process.

In the context of the present work, we can note that the added stabilization afforded by α-fluorine substituents is significantly less for a C–C bond than for a corresponding C–O bond.[40] A theoretical study of the reactions of oxygen-centered radicals with the fluoro olefins is clearly warranted.

Experimental Section

^{1}H NMR spectra were obtained on a Bruker WM250 spectrometer. Deuteriochloroform was used as solvent, and chemical shifts are reported in ppm downfield from internal tetramethylsilane. Chemical shifts are rounded to the nearest 0.01 ppm and coupling constants to the nearest 0.5 Hz. Chemical ionization mass spectra (CIMS) were obtained on a Finnegan 3300 spectrometer. Methane was used as the reagent gas. All high-resolution CIMS were obtained on a JEOL DX303 spectrometer equipped with a JMA5000 data system except those for compounds **4f**, **4g**, **4j**, **4k**, and **4m**, which were provided by Monash University. High-performance liquid chromatography (HPLC) was performed with a Du Pont 8800 instrument equipped with a variable-wavelength UV detector, which was coupled to a Trivector Trilab Model II data station. A Beckman Ultrasphere ODS column (250 × 25 mm) was employed with either acetonitrile/water or methanol/water as the eluent.

4-(1-Naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (1). A solution of 1-naphthoyl chloride (1.03 g, 5.4 mmol) in pyridine (1 mL) was added dropwise to a stirred solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (760 mg, 4.3 mmol) in pyridine (5 mL) at 0 °C. The mixture was allowed to stir for 18 h when water (0.5 mL) was added, and the mixture was stirred for a further 30 min. The mixture was then poured into ice water and extracted with ethyl acetate. The extracts were washed with dilute HCl, saturated $NaHCO_3$, water, and brine and dried (Na_2SO_4), and the solvent was evaporated. The crude nitroxide was recrystallized from ethyl acetate to give 4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl[43] as orange crystals (1.0 g, 57%), mp 101–102 °C. A second crop (0.7 g, 38%) had mp 100–101 °C and was indistinguishable from the first crop by HPLC.

Trapping Experiments. The radical trapping technique has been described previously.[16] A typical procedure is as follows.

The styrene(s) (**2a–m**) in benzene were added to an ampoule containing the appropriate amount of nitroxide (**1**) and di-*tert*-butyl peroxalate, and the resultant solution was degassed by three freeze–thaw cycles at 10^{-2} mmHg. The ampoule was then sealed in vacuo and heated in a constant temperature water bath at 60.0 (±0.1) °C for 90 min. The contents of the ampoule were analyzed by reverse-phase HPLC. The alkoxyamines (**4a–m** and **5**) were isolated by preparative HPLC and their identity proved by ^{1}H NMR and high resolution CIMS. For details see the supplementary material.

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Registry No. 1, 95676-89-4; **2a**, 100-42-5; **2b**, 100-80-1; **2c**, 622-97-9; **2d**, 626-20-0; **2e**, 637-69-4; **2f**, 107-96-6; **2g**, 350-51-6; **2h**, 405-99-2; **2i**, 2039-85-2; **2j**, 1073-67-2; **2k**, 586-39-0; **2l**, 100-13-0; **2m**, 2350-89-2; **4a**, 118921-69-0; **4b**, 118949-40-9; **4c**, 118921-70-3; **4d**, 118921-71-4; **4e**, 118921-72-5; **4f**, 118921-73-6; **4g**, 118921-74-7; **4h**, 118921-75-8; **4i**, 118921-76-9; **4j**, 118921-77-0; **4k**, 118921-78-1; **4l**, 118921-79-2; **4m**, 118921-80-5; $(CH_3)_3C{-}O^{\bullet}$, 3141-58-0; di-*tert*-butyl peroxalate, 1876-22-8; 1-naphthoyl chloride, 879-18-5; 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 2226-96-2.

Supplementary Material Available: Spectroscopic characterization of alkoxyamines (4 pages). Ordering information is given on any current masthead page.

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