The Measurement of Hammett ρ-Values for Homolytic Reactions by Electron Spin Resonance Spectroscopy: Reaction of t-Butoxyl Radicals with Substituted Anisoles

By **Alwyn G. Davies** * and **Jean-Paul Quintard**, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

The technique of steady-state e.s.r. spectroscopy has been used for determining the relative reactivity of ring-substituted anisoles towards t-butoxyl radicals at +25, 0, and −30 in $C_2Cl_3F_3$, at −55 in cyclo-C_3H_6, and at −73 and −94 °C in $CFCl_3$. The results show a good Hammett $\rho\sigma^+$ correlation, where ρ is given by the expression $\rho = -156/T$ (in K), and ρ (45 °C) −0.49. The correlation with σ is less satisfactory, when ρ (45 °C) = −0.52; previous studies by product analysis have given $\rho\sigma$ correlation with ρ −0.41, and the possible origin of this discrepancy is discussed. In 1 : 1 $Bu^tOH-C_2Cl_3F_3$ as solvent at −11 °C, $\rho = -0.74$, whereas in $C_2Cl_3F_3$ alone, $\rho = -0.59$.

WE have recently developed routes to a number of new radicals[1] and have become increasingly conscious of the need to devise more quantitative criteria by which the properties of radicals as reagents may be compared.

One such criterion is the Hammett ρ value which represents the response of the radical to substituents in its reaction with *meta*- or *para*-substituted compounds.[2]
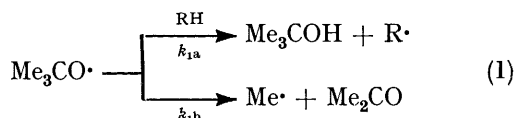
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[1] For example (a) $Me_3SiO\cdot$; P. G. Cookson, A. G. Davies, N. A. Fazal, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1976, **88**, 616; (b) $R_3C\overset{\bullet+}{O}H$; P. G. Cookson, A. G. Davies, B. P. Roberts, and M.-W. Tse, *J.C.S. Chem. Comm.*, 1976, 937; (c) heteroarylO·; A. G. Davies and R. Sutcliffe, unpublished work.

[2] Reviewed by (a) G. A. Russell, 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973; (b) I. B. Afanas'ev, *Russ. Chem. Rev.*, 1971, **40**, 216.

The value of ρ is obtained from the gradient of the plot of the logarithm of the relative reactivities of the substituted and unsubstituted compounds (log k_s/k_o) against the substituent constants σ (or σ^+).

There has however been a lot of controversy recently about the methods by which k_s/k_o is determined,[3] and about the interpretation of the ρ factors which have been obtained.[4]

The value of k_s/k_o has been derived from measurement (usually by g.l.c. or n.m.r.) of the formation of products or the consumption of reactants, but either method is subject to error if side reactions accompany the reaction which is to be followed.[3] We describe here the first application of the alternative technique of monitoring the concentrations of the intermediate radicals by e.s.r. spectroscopy; such a method should have some advantages over the established procedures, and a comparison of the results obtained by the two methods should be illuminating.

Because of its central importance in homolytic chemistry, we have chosen to study first the reactivity of the t-butoxyl radical, which for e.s.r. studies can conveniently be generated by the photolysis of di-t-butyl peroxide. The relative reactivities of substituted toluenes towards t-butoxyl radicals have been determined previously by analysis of the products which are formed when the hydrocarbons compete for chain reaction with t-butyl hypochlorite.[2] To avoid the criticism that some of the products might be formed by attack of chlorine atoms on the toluenes, Sakurai and Hosomi used instead di-t-butyl diperoxyoxalate at 45° as the (non-chain) source of t-butoxyl radicals, and determined relative reactivities from the ratio of t-butyl alcohol and acetone formed by reaction (1), giving a ρ value (against σ^+) of -0.35.[5]

$$\text{Me}_3\text{CO} \cdot \xrightarrow[\substack{\text{RH} \\ k_{1a}}]{} \text{Me}_3\text{COH} + \text{R} \cdot$$
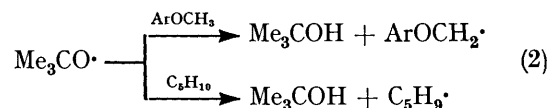$$\phantom{\text{Me}_3\text{CO} \cdot} \xrightarrow[k_{1b}]{} \text{Me} \cdot + \text{Me}_2\text{CO} \qquad (1)$$

The same technique was applied by Sakurai et al. to the reaction of a series of ring-substituted anisoles, which followed the $\rho\sigma$ relationship, with ρ -0.41.[6] Because of this high sensitivity of the reactivity towards the substituents, and because the e.s.r. spectra of the aryloxy-

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* We tried to use benzo-1,3-dioxole[7] as the reference compound, but it proved to be unsuitable because it is ca. 100 times as reactive as anisole. In cyclopropane at -60 °C, the radical o-$C_6H_4(O\dot{C}HO)$ showed $a(\text{H}\alpha)$ 23.66, $a(2\text{H})$ 0.41, and $a(2\text{H})$ 0.31 G.

[3] A. A. Zavitsas, G. Hanna, A. Arafat, J. Ogunwole, and L. R. Zavitsas, International Conference on Free Radicals, Aix-en-Provence, 1977, Abstracts, pp. 182—183.

[4] For example (a) A. A. Zavitsas and J. A. Pinto, J. Amer. Chem. Soc., 1972, 94, 7390; (b) W. A. Pryor, W. H. Davies, and J. P. Stanely, ibid., 1973, 95, 4754; (c) W. A. Pryor and W. H. Davies, ibid., 1974, 96, 7557; (d) R. W. Henderson and R. D. Ward, ibid., p. 7556; (e) R. W. Henderson, ibid., 1975, 97, 213; (f) W. H. Davis, J. H. Gleaton, and W. A. Pryor, J. Org. Chem., 1977, 42, 7; (g) W. H. Davis and W. A. Pryor, J. Amer. Chem. Soc., 1977, 99, 6365. A review of the current situation is given in references 3 and 4g.

methyl radicals under our working conditions are simpler than those of the arylmethyl radicals, we have chosen to use first the substituted anisoles as substrates; cyclo-

$$\text{Me}_3\text{CO} \cdot \xrightarrow[\substack{\text{ArOCH}_3 \\ \\ C_5H_{10}}]{} \begin{array}{l} \text{Me}_3\text{COH} + \text{ArOCH}_2 \cdot \\ \\ \text{Me}_3\text{COH} + \text{C}_5\text{H}_9 \cdot \end{array} \qquad (2)$$

pentane proved to be a suitable standard against which the rates could be compared [equation (2)].*

EXPERIMENTAL

The ring-substituted anisoles were either commercial products or were prepared by methylation of the corresponding phenols using methyl iodide and sodium hydroxide in dimethyl sulphoxide solvent.[7]

A typical preparation was as follows. Methyl iodide (5.7 g) was added to a solution of 3-chlorophenol (5.2 g) and sodium hydroxide (1.7 g) in dimethyl sulphoxide (30 cm³). The mixture was boiled under reflux for 2 h, then water was added, and the water–3-chloroanisole azeotrope (50 cm³) was distilled off. The azeotrope was extracted with ether, washed four times with aqueous sodium hydroxide to remove any residual phenol, and dried (Na₂SO₄). Distillation gave 3-chloroanisole (4.3 g, 75%), b.p. 85 °C at 20 mmHg.

4-Cyanoanisole was prepared from 4-bromoanisole and copper(I) cyanide.[8]

E.s.r. Technique.—Experiments were carried out using a Varian E4 e.s.r. spectrometer fitted with a Philips SP 500 W alternating current high pressure mercury lamp for photolysis within the cavity. The general kinetic method has been described previously.[9] The principal assumption in deriving ρ factors is that the rate constants for the removal of the various anisyl radicals from solution should be the same.

A solution of the appropriate anisole (ca. 1 mmol), cyclopentane (ca. 0.7 mmol), and di-t-butyl peroxide (ca. 1 mmol) in an inert solvent [1,1,2-trichloro-1,2,2-trifluoroethane, trichlorofluoromethane, cyclopropane, or a mixture of equal volumes of 1,1,2-trichloro-1,2,2-trifluoroethane and t-butyl alcohol (ca. 0.6 cm³)] was prepared in a silica e.s.r. tube by weighing. The concentrations of anisole and cyclopentane were chosen so that the areas of the peaks to be measured were approximately equal.

The solutions were then photolysed at various temperatures in the cavity of the spectrometer, using a modulation amplitude of 2 G so that the small hyperfine splittings by the ring protons in the anisyl radicals and by the γ-hydrogens in the cyclopentyl radicals were not resolved.

The superimposed spectra of the anisyl and cyclopentyl radicals were then recorded. For the measurement of relative intensities, the regions containing the fourth line of the cyclopentyl spectrum and the first line of the anisyl spectrum, and also (in case the spectra were polarised) the third line of the anisyl spectrum and the seventh line of the cyclopentyl spectrum were expanded on a ± 20 G scan. The first derivative spectra were integrated electronically, and

[5] H. Sakurai and A. Hosomi, J. Amer. Chem. Soc., 1967, 89, 458.

[6] H. Sakurai, A. Hosomi, and M. Kumada, J. Org. Chem., 1970, 35, 993.

[7] W. Bonthrone and J. W. Cornforth, J. Chem. Soc. (C), 1969, 1202.

[8] M. S. Newman and H. Boden, J. Org. Chem., 1961, 26, 2525.

[9] A. G. Davies, D. Griller, and B. P. Roberts, J. Chem. Soc. (B), 1971, 1823.

the ratios of the areas of the integrated lines were measured manually.

Four such measurements were carried out on each spectrum, and each experiment was carried out in duplicate.

The e.s.r. spectra of the ring-substituted anisyl radicals have been thoroughly discussed by Hudson and Root.[10] Data on the radicals (at -30 °C in $C_2Cl_3F_3$ solvent) which do not appear to have been reported before are as follows: 4-Me$_3$CC$_6$H$_4$OĊH$_3$, $a(2H_\alpha)$ 17.25, $a(2H_o)$ 0.55, $a(2H_m)$ 0.25 G; 3-ClC$_6$H$_4$OĊH$_2$, $a(2H_\alpha)$ 17.55, $a(2H_o)$ 0.60, $a(H_m)$ 0.23, $a(H_p)$ 0.43 G; 3,5-(MeO)$_2$C$_6$H$_3$OĊH$_2$, $a(2H_\alpha)$ 17.45, $a(2H_o)$ 0.58, $a(H_p)$ 0.33 G; 4-NCC$_6$H$_4$ĊH$_2$, $a(2H_\alpha)$ 17.90, $a(2H_o)$ 0.60, $a(2H_m)$ 0.27 G. 4-Cyanoanisole proved to be too insoluble in non-polar solvents to be suitable for kinetic measurements. The cyclopentyl radical, C$_5$H$_9$·, has $a(H_\alpha)$ 21.5, $a(4H_\beta)$ 35.2 G.

DISCUSSION

The results are summarised in Table 1, where rate constants are expressed on a per-hydrogen atom basis.

$k_3/k_4 = 0.91$. If we accept Walling's values (at 40 °C) of $k_4/k_5 = 0.66$,[11] and $k_5/k_6 = 1.20$,[12] Sakurai's results are

$$\log_{10}(k_3/k_6) = \log_{10}(A_3/A_6) + (E_6 - E_3)/2\,303RT \quad (7)$$

equivalent to $k_3/k_6 = 0.50$. The disparity between his value and ours is not surprising if only because of the cumulative errors in this approximation, but a further possible source of the difference is pointed out below.

If we accept for the value of k_6 (per hydrogen atom) expression (8) which has been used previously,[9] approximate values for the kinetic parameters of the reactions which we have studied can be derived. These are listed in Table 2.

$$k_6 = 1 \times 10^8\exp(-5\,200/RT)\,1\,\text{mol}^{-1}\,\text{s}^{-1} \quad (8)$$

A comparison between the ρ values which we and Sakurai obtain are more significant. Our results correlate better with σ^+ than σ values, and a typical plot (that for the reaction at 25 °C in $C_2Cl_3F_3$ solvent) is
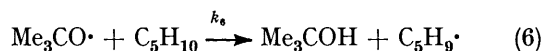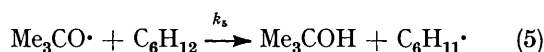
TABLE 1

Kinetics of abstraction of hydrogen atoms from ring-substituted anisoles: Hammett relationships using cyclopentane as standard [a,b]

Solvent	$C_2Cl_3F_3$	$C_2Cl_3F_3$	$C_2Cl_3F_3$	C_3H_6	$CFCl_3$	$CFCl_3$	Bu^{t}OH–$C_2Cl_3F_3$
T °C	$+25$	0	-30	-55	-73	-94	-11
$k(\text{PhOMe})/k(C_5H_{10})$	0.89	0.89	0.90	1.33	0.84	0.89	0.89
$k(XC_6H_4OMe)/k(C_6H_5OMe)$							
X = H	1	1	1	1	1	1	1
4-Bu^t	1.32	1.38	1.54	1.44	1.62	1.86	1.61
4-Cl	0.82	0.91	0.77	0.82	0.86	0.81	0.77
3-F	0.70	0.61	0.59	0.62	0.51	0.60	0.62
3-Cl	0.57	0.55	0.55	0.46	0.55	0.50	0.50
ρ (σ)	-0.57	-0.64	-0.70	-0.75	-0.81	-0.89	-0.80
s	(±0.08)	(±0.15)	(±0.10)	(±0.13)	(±0.12)	(±0.11)	(±0.09)
r	(0.97)	(0.95)	(0.95)[c]	(0.96)	(0.97)	(0.98)	(0.98)
ρ (σ^+)	-0.53	-0.61	-0.67	-0.70	-0.76	-0.83	-0.74
s	(±0.05)	(±0.04)	(±0.08)	(±0.07)	(±0.07)	(±0.06)	(±0.05)
r	(0.99)	(0.99)	(0.96)[c]	(0.99)	(0.99)	(0.99)	(0.99)

[a] The substituent constants (σ and σ^+) used were as follows: (4-Bu^t, -0.20 and -0.26; 4-Cl, $+0.23$ and ±0.11; 3-F, $+0.34$ and $+0.33$; 3-Cl, $+0.37$ and $+0.40$; 3-MeO, $+0.11$ and $+0.05$; 4-Br, $+0.23$ and $+0.11$). [b] The slope ρ of the regression line, the standard deviation (s) from that line, and the correlation coefficient (r) were calculated by the methods outlined by H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191. [c] The correlation coefficients here are poorer because the plots include points for 4-BrC$_6$H$_4$OMe [$k(XC_6H_4OMe)/k(C_6H_5OMe) = 0.82$], 3-MeOC$_6H_4$OMe [$k(XC_6H_4OMe)/k(C_6H_5OMe) = 0.77$], and 3,5-(MeO)$_2C_6H_3$OMe [$k(X_2C_6H_3OMe)/k(C_6H_5OMe) = 0.88$]. These points deviated from the least squares plot, perhaps because the reactants had a low solubility, and the compounds were therefore omitted in the other experiments.

A rough comparison between Sakurai's rates [6] and ours can be derived from a knowledge of the relative rates of reactions (3)—(6). An Arrhenius plot of

$$Me_3CO\cdot + PhOCH_3 \xrightarrow{k_3} Me_3COH + PhOĊH_2 \quad (3)$$

$$Me_3CO\cdot + PhCH_3 \xrightarrow{k_4} Me_3COH + PhĊH_2 \quad (4)$$

$$Me_3CO\cdot + C_6H_{12} \xrightarrow{k_5} Me_3COH + C_6H_{11}\cdot \quad (5)$$

$$Me_3CO\cdot + C_5H_{10} \xrightarrow{k_6} Me_3COH + C_5H_9\cdot \quad (6)$$

expression (7), based on our three results in $C_2Cl_3F_3$ solvent gives $A_3/A_6 = 0.56$, $E_6 - E_3 = -280$ cal mol^{-1}, and k_3/k_6 at 45° $= 0.87$. Sakurai reports that at 45 °C,

shown in Figure 1. For an isoentropic series of reactions a plot of ρ against $1/T$ should be linear passing through the origin,[13] and Figure 2 shows that this correlation is satisfactory with $\rho = 156/T$: indeed ρ values determined

TABLE 2

Approximate kinetic parameters (per hydrogen atom) for the abstraction of hydrogen from ring-substituted anisoles, XC$_6$H$_4$OCH$_3$

X	H	4-Bu^t	4-Cl	3-F	3-Cl
$\log_{10}(A/1\,\text{mol}^{-1}\,\text{s}^{-1})$	7.74	7.56	7.78	7.74	7.60
$E/\text{kcal mol}^{-1}$	4.9	4.48	5.03	5.14	5.04
$10^{-4}k/1\,\text{mol}^{-1}\,\text{s}^{-1}$ at 45°	2.35	2.99	2.09	1.60	1.40

at -55 °C in cyclopropane solvent, or at -73 and -94 °C in CFCl$_3$ solvent do not deviate far from the line

[10] A. Hudson and K. D. J. Root, *J. Chem. Soc. (B)*, 1970, 656.
[11] C. Walling and B. Jackson, *J. Amer. Chem. Soc.*, 1960, **82**, 6108.

[12] P. Wagner and C. Walling, *J. Amer. Chem. Soc.*, 1965, **87**, 5178.
[13] P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

established for the reaction in $C_2Cl_3F_3$ at $+25$, 0, and $-30\,°C$. At $+45\,°C$ in $C_2Cl_3F_3$, our results give ρ -0.49
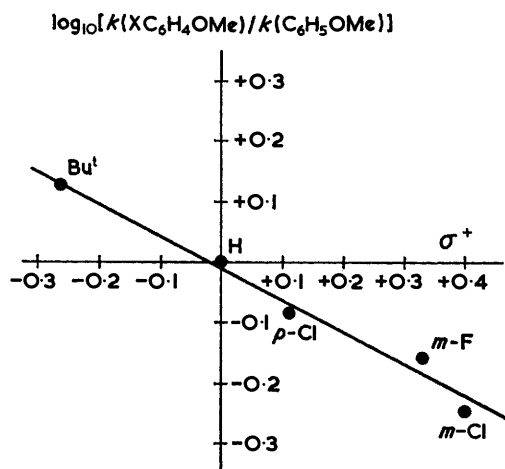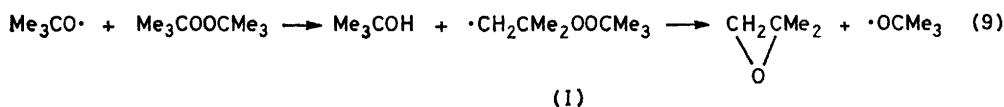
$$\log_{10}[k(XC_6H_4OMe)/k(C_6H_5OMe)]$$

FIGURE 1 Hammett plot of log $k_{rel.}$ for hydrogen abstraction from substituted anisoles in $C_2Cl_3F_3$ solvent at 25 °C

(against σ^+) or -0.52 (against σ); under the same conditions, Sakurai [6] obtained ρ -0.41 (against σ).

and they applied a correcting factor of 0.14—0.16 in $ca.$ 1—2.65 units of k_{1a}/k_{1b}.

We doubt however whether reaction at ring hydrogen is significant. If it were to occur it would presumably involve first addition of the t-butoxyl radical to the aromatic ring to give a cyclohexadienyl radical, but no such radical could be detected in our e.s.r. spectra.[14] On the other hand, the formation of t-butyl alcohol by the attack of t-butoxyl radicals on the parent di-t-butyl diperoxyoxalate may well be significant, and indeed Sakurai's results show that when the peroxyoxalate is decomposed in $C_2Cl_3F_3$ in the absence of anisole, t-butyl alcohol is formed in $ca.$ 12% yield.[15] The equivalent reaction under our conditions would be the formation of the β-peroxyalkyl radical (I), but the properties of this radical are well known.[16]

Its hyperfine coupling constants $[a(2H_\alpha)$ 21.4, $a(6H_y)$ 1.2 G] are such that its spectrum would not interfere with the lines of the anisyl or cyclopentyl radicals which we use for measuring the kinetics. At the temperatures of our experiments, radical (I) would rapidly ring-close to give 2,2-dimethyloxiran and t-butoxyl radicals, but this would not affect our results.

$$Me_3CO\cdot \ + \ Me_3COOCMe_3 \ \longrightarrow \ Me_3COH \ + \ \cdot CH_2CMe_2OOCMe_3 \ \longrightarrow \ \underset{O}{\underset{\diagdown/}{CH_2CMe_2}} \ + \ \cdot OCMe_3 \quad (9)$$

$$(I)$$

The origin of this difference may lie in the occurrence of side reactions which must be allowed for if relative reactivities in one particular process are to be determined
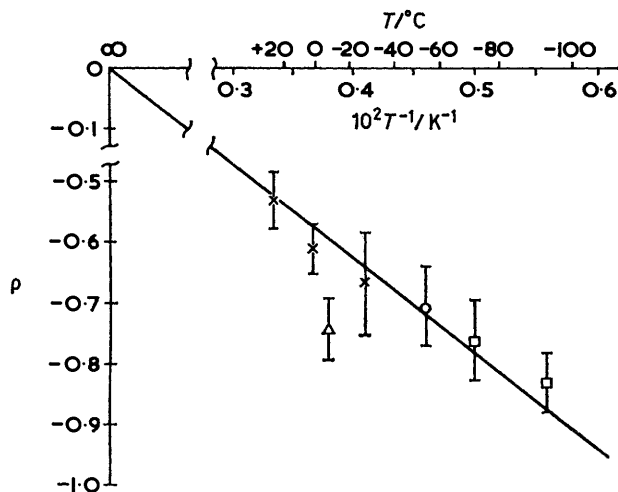

FIGURE 2 Plot of ρ against $1/T$. Solvent: $\times$, $C_2Cl_3F_3$; $\bigcirc$, cyclo-C_3H_6; $\square$, $CFCl_3$; $\triangle$, $1:1$ Bu^tOH–$C_2Cl_3F_3$

from the analysis of products. Sakurai and his co-workers attempted to allow for the origin of t-butyl alcohol by attack on ring hydrogen atoms by using diphenyl ether and chlorobenzene as model substrates,
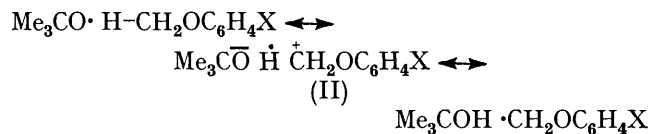
We believe that this e.s.r. technique of measuring the concentrations of the relevant radical intermediates has some advantages over the established methods of measuring the concentrations of reactants or reaction products,[3] and that it should prove to be very useful for determining the ρ factors of radical reactions. One particular type of reaction to which this method could be applied is that in which the radicals to be studied ($e.g.$ $R_3C\overset{+}{O}H$) [1b] can as yet be generated only photolytically.

The dispute about the significance of ρ factors has been concerned with the degree to which they reflect the bond dissociation energies of the reactants, or the partial charges which may be developed in the transition states. In early studies the former factor was largely ignored,[2a] but Zavitsas [4b] has argued that there is no evidence for the polar effect in hydrogen abstraction, and that the relative reactivities are controlled only by the effect of the substituents on the dissociation energies of the CH bonds, and the degree to which those bonds are broken in the transition states. Pryor [4b,c,g] and Henderson [4d,e] have reported that the abstraction of hydrogen from toluenes by certain alkyl radicals results in a $positive$ ρ value, thus providing evidence for a polar effect, but Zavitsas [3] has argued that their experimental method is invalidated by the addition of alkyl radicals to the aromatic nucleus.

In the context of the reactions which we have been

[14] P. G. Cookson, A. G. Davies, and B. P. Roberts, $J.C.S.$ $Chem. Comm.$, 1976, 289.

[15] Ref. 6, Figure 1.

[16] A. J. Bloodworth, A. G. Davies, I. M. Griffin, B. Muggleton, and B. P. Roberts, $J.$ $Amer. Chem. Soc.$, 1974, 96, 7599.

studying, the question is the degree to which the polar canonical form (II) may contribute to the structure of the transition state, and be stabilised by electron release from the substituent X.

$$Me_3CO\cdot \; H-CH_2OC_6H_4X \longleftrightarrow$$

$$Me_3C\overline{O} \; \overset{+}{H} \; \overset{\cdot}{C}H_2OC_6H_4X \longleftrightarrow$$

$$(II)$$

$$Me_3COH \cdot CH_2OC_6H_4X$$

Evidence for this transition state polarity might be obtained by changing the polarity of the solvent,[5,17] and the ρ value for the reaction was therefore determined at -11 °C using $1:1$ t-butyl alcohol–$C_2Cl_3F_3$ as the medium. The value obtained was -0.74, significantly

[17] *Cf.* E. M. Kosower and I. Schwager, *J. Amer. Chem. Soc.*, 1964, **86**, 5528.

greater than that of -0.59 measured in $C_2Cl_3F_3$ alone as solvent. This would be compatible with the polar form (II) making an increasing contribution to the structure of the transition state as the electron-releasing power of the substituent is increased, but it might also be ascribed to solvation of the t-butoxyl radical making it more ' electrophilic,' less reactive, and more discriminating in its reactions.

We hope to examine this question further by the application of the e.s.r. technique to other systems.