

# LINEAR FREE ENERGY RELATIONSHIPS IN RADICAL REACTIONS. II.\* HYDROGEN ABSTRACTION FROM SUBSTITUTED TOLUENES BY *TERT*-BUTYL, *TERT*-BUTOXYL AND *TERT*-BUTYLPEROXYL RADICALS

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Calculations were carried out to study the validity of  $\sigma$ -scales for hydrogen abstraction from substituted toluenes by *tert*-butyl, *tert*-butoxyl and *tert*-butylperoxyl radicals. Rate constants were compiled and evaluated from the literature for *meta*- and/or *para*-substituted toluenes. The substituents were characterized by factored ionic sigmas ( $\sigma_1, \sigma_R, \sigma_R^\ddagger$ ), ionic scales ( $\sigma, \sigma^+$ ) and various radical sigmas ( $\sigma^\cdot$ ). The dependence of  $\log k$  values on these substituent descriptors was investigated using 'stepwise linear regression' and 'all possible regression' methods. The following predictive equations can be recommended:

for *tert*-butyl radicals, at 321 K:

$$\log k_1 = 1.024 + 0.776\sigma_1 + 0.653\sigma^\cdot \quad (R = 0.8137)$$

for *tert*-butoxyl radicals, at 313 K:

$$\log k_2 = 5.529 - 0.623\sigma^+ \quad (R = 0.9376)$$

and for *tert*-butylperoxyl radicals, at 303 K:

$$\log k_3 = -1.410 - 0.810\sigma + 0.337\sigma^\cdot \quad (R = 0.9628)$$

The results suggest that there is no universal radical scale for hydrogen abstraction reactions, that the rate is primarily influenced by polar factors (inductive, resonance) and that only two radical scales ( $\sigma^\cdot$  and  $\sigma_\alpha^\cdot$ ) are appropriate, showing a small, yet significant, role of radical stabilization.

## INTRODUCTION

There has been continuing interest in the mechanism of the title reactions in recent decades. Although many Hammett-type correlations have been reported,<sup>1–14</sup> even the suitability of the Hammett equation for radical reactions is still questionable, and the scale to be used for radical reactions is still a matter of controversy. Pryor *et al.*<sup>9</sup> allowed (Brown–Okamoto)  $\sigma^+$  to be 'marginally' better empirically, emphasizing, however, that 'there is no reason to assume that the extra resonance for radical reaction is accurately measured by the  $\sigma^+$  scale.' According to Jones *et al.*,<sup>15</sup> 'It is generally found that the use of  $\sigma^+$  gives a substantially better correlation for radical reactions.' Hansch and Leo<sup>16</sup> proposed to

use ionic  $\sigma$ -s according to empirical experience.<sup>16</sup> Although several 'radical sigma'  $\equiv \sigma^\cdot$  (sigma dot) scales have already been defined,<sup>17–20</sup> none of them has found general use and there are still tremendous efforts to be made to establish a proper one. (The present author is well aware of the existence of other  $\sigma^\cdot$  scales, but the small number of substituents limits their use.) Finally, statistically significant correlations can be found using factored (ionic) sigmas ( $\sigma_1, \sigma_R, \sigma_R^\ddagger$ ) for hydrogen abstraction reactions by peroxyl radicals [21].

Therefore, the aim of this work was (i) to evaluate rate constants for the title reactions, (ii) to classify the radicals and/or reactions, (iii) to prove the usefulness of factored sigmas in radical reactions and (iv) to compare the various scales and determine the best possible one.

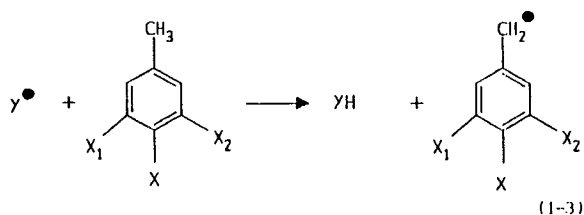
\* For Part I, see Ref. 21. This paper was presented at the 6th International Symposium on Organic Free Radicals, Nordwijkerhout, The Netherlands, 23–28 August 1992.

Our earlier investigations on substituted benzyl radicals<sup>22</sup> make it probable that there is no 'universal' radical sigma ( $\sigma^{\cdot}$ ) scale at all, but sigma scale(s) still might be applied for a definite class of reactions, such as hydrogen transfer. Consequently, this study is limited to hydrogen abstraction reactions, being one of the best known, well characterized reaction classes. However, it is difficult to find data sufficient for a detailed statistical analysis. Several papers give Hammett relationships for relative rate constants only, and complications are caused by systematic errors and the fact that the measurements were performed at different temperatures. Therefore, evaluated rate constant values are needed first. Another interesting question is whether the Hammett relationships published so far remain valid after careful analysis. As is well known, the average number of points (substituents) in Hammett correlations is as small as  $6 \pm 2$  (!),<sup>9</sup> which enhances the possibility of finding correlation by chance.

It should be mentioned that after this analysis poorer correlations can be expected because of (i) systematic errors (interlaboratory reproducibility) and (ii) suspect data correction or outlier rejection in individual determinations. Moreover weaker correlations are expected for radical than for ionic reactions. Because of the smaller effects, the slopes, i.e. the reaction constants ( $\rho$ ) are close to zero. This problem can be overcome only by including a large number of compounds (substituents) in the study. If sufficient degrees of freedom are ensured, justified answers to the problems outlined seem possible.

#### EVALUATION OF RATE CONSTANTS AND METHOD OF CALCULATION

Rate constants were collected from the literature for the following reactions:



where (1)  $Y = \textit{tert}$ -butyl  $\equiv$  1,1-dimethylethyl (1605-73-8), (2)  $Y = \textit{tert}$ -butoxyl  $\equiv$  1,1-dimethylethoxyl (3141-58-0) and (3)  $Y = \textit{tert}$ -butylperoxyl  $\equiv$  1,1-dimethylethyldioxyl (3395-62-8) radicals.

All values available were taken into account. Relative values were converted into absolute values using reliable reference values<sup>12,23-25</sup> The rate constants were transformed to the same temperature, either using the

reference value directly measured by Munger<sup>25</sup> for *tert*-butyl or applying an average activation energy of  $E_a = 13.11 \pm 5.45 \text{ kJ mol}^{-1}$  ( $n = 17$ )<sup>26</sup> for *tert*-butoxyl radical. For the same elementary steps, all the rate constant values (belonging to different literature sources, various systems, solvents, etc.) were averaged without outlier rejection. Thus the standard errors of the rate constants were different, depending on the quality of data and the number of values averaged. The mean standard error was  $38 \pm 19\%$  ( $15 \pm 8.5\%$  for *tert*-butyl and  $31 \pm 8.2\%$  for the oxygen-centred radicals). The sigma constants  $\sigma_1$ ,  $\sigma_R$  and  $\sigma_R^+$  were those of Charton.<sup>27</sup> They represent a separation (factorization) of the original Hammett  $\sigma$  and the Brown-Okamoto  $\sigma^+$  into inductive and resonance (or rather localized and delocalized) terms. Values of  $\sigma$  and  $\sigma^+$  were taken from the monograph of Hansch and Leo,<sup>16</sup> defined on the basis of the reactivity for *para*-substituted benzoic acid in water and of the solvolysis of cumyl chloride in 90% acetone, whereas  $\sigma^{\cdot}$  scales are from Refs 17-20. Note that  $\sigma^+$  values often vary considerably with the literature source. Throughout this study average  $\sigma^+$  values listed in Ref. 16 were used. Only scales having at least nine substituents were taken into account. It must be kept in mind that the different  $\sigma$  sets are correlated, and have an either-or relationship with each other. That is, either  $\sigma$  or  $\sigma^+$  or factored sigmas ( $\sigma_1$ ,  $\sigma_R$ ,  $\sigma_R^+$ ) should be used in the model separately, even if they provided a better description together. Evaluated rate constants and sigma values are summarized in Table 1.

Table 1 includes all of the data in the literature; if there are omissions the author would appreciate being informed. At the moment, filling of the empty positions of the data matrix is not possible. The question marks indicate the urgent need to measure rate constants and sigmas. The relationship between  $\log k_i$  ( $i = 1, 2, 3$ ) and  $\sigma_1, \sigma_R, \dots, \sigma_D$  (see Table 1) was investigated in the form of

$$\log k_i = \rho_0 + \rho_1\sigma_1 + \rho_R\sigma_R + \dots + \rho_C\sigma_C + \dots + \rho_D\sigma_D \quad (4)$$

using 'stepwise linear regression' and 'all possible regression' analysis.<sup>35</sup> The calculations were carried out using the DrugIdea program package<sup>36</sup> developed for quantitative structure - activity relationship studies on an IBM PC XT/AT. A double 5% significance level (include/remove variables in/from the model) was accepted. Searching solutions as linear functions for  $\log k$  involves the assumption of constant proportional error in  $k$ . Although this was not examined (lack of repeated data), this assumption is generally accepted. During the calculations the largest data set was applied, including gradually more scales and ignoring the rate constants for which no sigma values exist. This, however, may lead to different conclusions according to the number of points involved in the analysis, and therefore only the unambiguous conclusions are reported here. Assigning zeros for *meta* substituents in the '*para*'

Table 1. Evaluated rate constants for hydrogen abstraction reactions from *meta*-X<sub>1</sub>-X<sub>2</sub> and/or *para* X-substituted toluenes by *tert*-butyl (*k*<sub>1</sub>), *tert*-butoxyl (*k*<sub>2</sub>) and *tert*-butylperoxyl (*k*<sub>3</sub>) radicals at 48, 40 and 20 °C, respectively, together with sigma values of substituents

Substituents			Rate constants (l mol <sup>-1</sup> s <sup>-1</sup> )										Sigma scales				
No.	X <sub>1</sub>	X <sub>2</sub>	X	k <sub>1</sub>	k <sub>2</sub> × 10 <sup>-5</sup>	k <sub>3</sub> × 10 <sup>2</sup>	σ <sub>1</sub> <sup>a</sup>	σ <sub>R</sub> <sup>a</sup>	σ <sub>R</sub> <sup>+</sup>	σ <sup>b</sup>	σ <sup>+b</sup>	σ <sub>σ</sub> <sup>c</sup>	σ <sup>c,d</sup>	σ <sub>PM</sub> <sup>e</sup>	σ <sup>d,g</sup>		
1	H	H	CH <sub>3</sub> O	28·0 <sup>h</sup>	9·14 <sup>i</sup>	8·3 <sup>j</sup>	0·3	-0·58	-0·66	-0·27	-0·78	0·018	0·24	0·43	-0·12	-0·29	
2	H	H	<i>t</i> -Bu	12·4 <sup>k</sup>	?	?	-0·01	-0·18	-0·13	-0·20	-0·29	0·008	0·13	?	?	?	
3	H	H	CH <sub>3</sub>	10·3 <sup>l</sup>	5·41 <sup>m</sup>	5·02 <sup>n</sup>	-0·01	-0·16	-0·16	-0·27	-0·31	0·015	0·11	0·39	-0·02	-0·10	
4 <sup>o</sup>	CH <sub>3</sub>	CH <sub>3</sub>	H	11·5 <sup>l</sup>	3·89 <sup>p</sup>	?	-0·02	-0·32	-0·32	-0·14	-0·16	?	0·07	?	?	?	
5	H	H	CH <sub>3</sub>	10·5 <sup>l</sup>	4·59 <sup>r</sup>	3·5 <sup>j</sup>	-0·01	-0·16	-0·16	-0·07	-0·08	-0·002	0·03	?	?	?	
6	H	H	PhO	52·4 <sup>h</sup>	5·32 <sup>s</sup>	6·6 <sup>j</sup>	0·40	-0·48	-0·48	-0·03	-0·51	0·018	?	?	?	?	
7	H	H	H	10·1 <sup>l</sup>	3·23 <sup>u</sup>	5·97 <sup>v</sup>	0	0	0	0	0	0	0	0	0	0	
8	H	H	F	17·4 <sup>z</sup>	?	?	0·54	-0·48	-0·37	0·06	-0·011	-0·08	0·12	-0·25	-0·24	-0·08	
9	H	H	Ph	?	6·95 <sup>x</sup>	?	0·12	-0·11	-0·17	0·1	-0·21	?	0·46	0·42	0·12	0·07	
10	H	H	CH <sub>3</sub> O	28·9 <sup>h</sup>	?	?	0·30	-0·58	-0·58	0·12	0·07	-0·001	-0·02	?	?	?	
11	H	H	Cl	22·1 <sup>l</sup>	3·09 <sup>y</sup>	3·0 <sup>j</sup>	0·47	-0·25	-0·21	0·23	0·12	0·011	0·12	0·18	0·08	0·08	
12	H	H	Br	34·9 <sup>z</sup>	2·29 <sup>aa</sup>	?	0·47	-0·25	-0·19	0·23	0·16	?	0·13	0·20	0·17	0·20	
13	H	F	H	17·5 <sup>ab</sup>	?	?	0·54	-0·48	-0·37	0·34	0·37	-0·009	-0·05	?	?	?	
14	H	Cl	H	15·6 <sup>ac</sup>	2·34 <sup>ad</sup>	1·85 <sup>j</sup>	0·47	-0·25	-0·21	0·37	0·40	-0·007	-0·04	?	?	?	
15	H	Br	H	31·8 <sup>z</sup>	?	?	0·47	-0·25	-0·19	0·39	0·39	?	?	?	?	?	
16	H	H	CO <sub>2</sub> Me	52·9 <sup>h</sup>	?	?	0·32	0·11	0·11	0·45	0·49	0·043	0·35	?	?	?	
17	H	H	Ac	?	?	?	0·30	0·20	0·06	0·50	?	0·060	?	?	?	?	
18	H	CN	H	23·2 <sup>h</sup>	2·14 <sup>ae</sup>	1·1 <sup>j</sup>	0·63	0·08	0·08	0·56	0·56	-0·026	-0·12	?	?	0·61	
19 <sup>o</sup>	H	Cl	Cl	25·7 <sup>ac</sup>	?	?	0·94	-0·50	-0·38	0·60	0·52	?	?	?	?	?	
20	H	H	CN	48·2 <sup>af</sup>	1·52 <sup>ag</sup>	1·4 <sup>j</sup>	0·63	0·08	0·08	0·66	0·67	0·040	0·46	0·41	0·34	0·46	
21	H	NO <sub>2</sub>	H	71·3 <sup>z</sup>	0·937 <sup>ah</sup>	1·05 <sup>j</sup>	0·67	0·10	0·10	0·71	0·69	?	-0·11	?	?	?	
22	H	H	NO <sub>2</sub>	?	0·808 <sup>ah</sup>	1·45 <sup>j</sup>	0·67	0·10	0·10	0·78	0·70	?	0·57	0·76	0·27	0·43	

<sup>a</sup> Factored sigmas from Ref. 27.

<sup>b</sup> Hammett and Brown-Okamoto  $\sigma^+$  scale from Ref. 16.

<sup>c</sup> Arnold-Dust-Wayner scale from Ref. 20.

<sup>d</sup> Creary scale from Ref. 19.

<sup>e</sup> Agirbas-Dincirk-Jackson-Towson scale for *para* substituents only, from Ref. 18.

<sup>f</sup> Fisher-Meierhofer  $\sigma^+$  scale for *para* substituents only, from Ref. 17.

<sup>g</sup> Ref. 28; Dreshem remeasured and recalculated the original Fisher-Meierhofer  $\sigma^+$  values.

<sup>h</sup> From Ref. 29.

<sup>i</sup> Refs 3 and 5.

<sup>j</sup> Ref. 7.

<sup>k</sup> Refs 12, 13, 23 and 25.

<sup>l</sup> Refs 10, 12, 13, 24 and 28.

<sup>m</sup> Refs 2-5 and 30.

<sup>n</sup> Statistically corrected for one methyl group, from Refs 7 and 31.

<sup>o</sup> For disubstituted toluenes the sum of the respective sigmas are listed and used.

<sup>p</sup> Corrected for one methyl group, Ref. 24.

<sup>q</sup> Refs 2-5, 30 and 32.

<sup>r</sup> Refs 2-4.

<sup>s</sup> Refs 12, 23 and 24.

<sup>t</sup> Ref. 24.

<sup>u</sup> Refs 7, 33 and 34.

<sup>v</sup> Using as basis *k*<sub>2</sub> (*t*-BuO<sup>·</sup> + ethylbenzene and cumene also), Refs 1 and 2.

<sup>w</sup> Using as basis *k*<sub>2</sub> (*t*-BuO<sup>·</sup> + ethylbenzene and cumene also), Refs 1-4 and 30.

<sup>x</sup> Usually Ref. 10; for *para*-fluoro compound (8) Refs 10, 12 and 14.

<sup>aa</sup> Ref. 2.

<sup>ab</sup> Refs 12 and 25.

<sup>ac</sup> Refs 12, 13, 23 and 25.

<sup>ad</sup> Using as basis *k*<sub>2</sub> (*t*-BuO<sup>·</sup> + ethylbenzene and cumene also), Refs 1-5 and 30.

<sup>ae</sup> Ref. 5.

<sup>af</sup> Refs 10, 12, 23 and 25.

<sup>ag</sup> Refs 2-5.

<sup>ah</sup> Ref. 3.

scales ( $\sigma_j$ ,  $\sigma_{FM}^+$ ,  $\sigma_D^+$ ) is an alternative possibility, which makes manipulation of large data sets feasible, but, in fact, it does not increase the degrees of freedom.

## RESULTS AND DISCUSSION

### Hydrogen abstraction by *tert*-butyl radical from toluenes

A simple linear equation with any of the independent variables (sigmas from Table 1) provides a poor description, and only the inductive (and Hammett) sigma passes the significance limit:

$$\log k_1(48^\circ\text{C}) = 1.14 + 0.597\sigma_1 \quad (5)$$

$$n = 19; R = 0.6250; F = 10.90;$$

$$p < 0.421\%; s = 0.213$$

where  $n$  is the number of points (rate constants) involved,  $R$  is the (multiple) correlation coefficient,  $F$  is the overall Fisher statistic,  $p$  is the significance of  $F$  and  $s$  is the standard error of the estimate. By including a second variable into the model, more equations can be obtained which meet the criterion of 5% significance. The stepwise linear regression technique has selected double linear relationship for  $\sigma$  and  $\sigma^+$ , which is hard to justify theoretically. While holding similar information,  $\rho$  and  $\rho^+$  have opposite signs, indicating nucleophilic and electrophilic character simultaneously! This contradictory behaviour is understandable, since subtracting the resonance part from sigma leaves the inductive contribution [see equation (5)]. Because of the intercorrelation of  $\sigma$  and  $\sigma^+$ , the following equation is recommended for prediction purposes:

$$\log k_1(48^\circ\text{C}) = 1.024 + 0.776\sigma_1 + 0.653\sigma_c^+ \quad (6)$$

$$n = 16; R = 0.8137; F = 12.73;$$

$$p < 0.093\%; s = 0.169$$

For *para* substituents alone, this combination ( $\sigma_1$ ,  $\sigma_c^+$ ) is even better. One more combination of variables ( $\sigma_1$ ,  $\sigma_a^+$ ) has passed the significance limit:

$$\log k_1(48^\circ\text{C}) = 1.08 + 0.760\sigma_1 + 3.74\sigma_a^+ \quad (7)$$

$$n = 14; R = 0.7849; F = 8.83;$$

$$p < 0.53\%; s = 0.257$$

Further combinations were found to be inappropriate. As *tert*-butyl is a prototype of nucleophilic radicals, for hydrogen abstraction reactions by such radicals a reasonable description can be expected from the inductive scale together with Creary's  $\sigma^+$  scale (or perhaps  $\sigma_1$  with  $\sigma_a^+$ ). Although all the above statistics are significant even at the 0.5% level (and these are the best possible fits using these rate constants evaluated), Figure 1 shows that the fit is poor. Clustering of the points increases the probability of correlation by

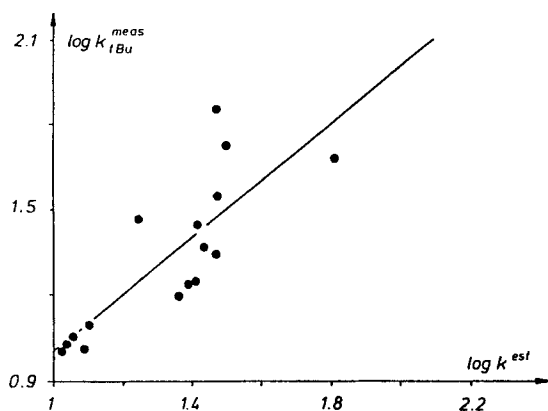


Figure 1. Measured (evaluated) vs calculated [by equation (6)] rate constants for hydrogen abstraction by *tert*-butyl radicals from substituted toluenes at 321 K

chance. The present error level (interlaboratory reproducibility) does not allow one to achieve a better description. According to some early literature sources,<sup>6,37</sup> the positive  $\rho$  for hydrogen abstraction from toluenes by *tert*-butyl radical is not due to the 'polar effect' at all, being rather an artefact ( $\rho$  reflects differences in the bond dissociation energy of substituted toluenes, i.e. it cannot be positive,<sup>6</sup> and the yield of hydrogen abstraction product is directly controlled by the viscosity of the solvent<sup>37</sup>). Recent investigations<sup>12,25,38</sup> undoubtedly prove the strong nucleophilic character of *tert*-butyl radical. Therefore, a positive correlation (Figure 1) is expected and thus the weak correlation observed has not only statistical but also physical significance.

### Hydrogen abstraction by *tert*-butoxyl radical from toluenes

Unlike *tert*-butyl, *tert*-butoxyl radicals yield much better correlations with a simple linear equation. Three radical scales ( $\sigma_a^+$ ,  $\sigma_c^+$ ,  $\sigma_j$ ), however, do not reach the significance level. The best description can be accomplished by  $\sigma^+$ :

$$\log k_2(40^\circ\text{C}) = 5.53 - 0.622\sigma^+ \quad (8)$$

$$n = 14; R = 0.9376; F = 87.31;$$

$$p < 0.00015\%; s = 0.112$$

and a not significantly worse one by using  $\sigma$ .

For *para* substituents alone even the Dreshem (or Fisher–Meierhofer) scale provides a reasonable fit:

$$\log k_2(40^\circ\text{C}) = 5.63 - 1.24\sigma_D^+ \quad (9)$$

$$n = 8; R = 0.9030; F = 26.49;$$

$$p < 0.24\%; s = 0.162$$

Inclusion of a second variable in the model does not really worsen the significance of the correlations. Rigorous treatment of the stepwise linear regression procedure, however, removes any second variable, keeping  $\sigma^+$  only. The best candidate for a second variable is  $\sigma_{\text{R}}^+$ , but its inclusion in the equation is significant only at the 20% level. In contrast, factored sigmas yield true double linear relationships, of which the best one is

$$\log k_2(40^\circ\text{C}) = 5.54 - 0.564\sigma_{\text{I}} - 0.828\sigma_{\text{R}}^+ \quad (10)$$

$n = 14; R = 0.9113; F = 26.93;$   
 $p < 0.0077\%; s = 0.139$

Other combinations, however, do not increase the quality of description, and radical scales yield a poorer correlation. To gain a deeper insight into the mechanism of the reaction, equation (10) is recommended, whereas equation (8) gives a better description. The quality of fit can be seen in Figure 2.

Jones *et al.*<sup>15</sup> reported weak correlations with one variable ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_{\text{R}}^+$ ,  $\sigma_{\text{I}}$  or  $\sigma_{\text{C}}^+$  alone) for *tert*-butoxyl radical additions to substituted styrenes and excellent correlations with two variables (one ionic  $\sigma$  and one radical  $\sigma^+$ ), in contrast to the observations in this work. Jones *et al.* correlated relative rate constants, hence the constant term (the intercept) has no real physical significance in their equations, although it improves the fit. Moreover, the small number of data involved in their study ( $n = 4-5$  for *meta*, 7 for *para* and 10-13 for all substituents, with omission of the *p*-nitro point) implies a risk of finding accidental relationships. Re-

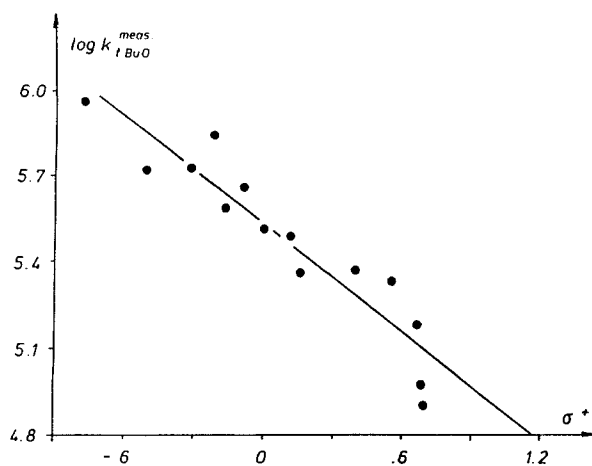


Figure 2. Measured (evaluated) rate constants vs Brown–Okamoto  $\sigma^+$  for hydrogen abstraction by *tert*-butoxyl radicals from substituted toluenes at 313 K. The line is defined by equation (8)

evaluation of the data of Jones *et al.* with all scales used in this study gives a three-variable relationship without a constant term, which cannot be interpreted, however, because of the strong intercorrelation of the variables. Although it might happen that the substituent scales behave oppositely according to the reaction class being addition or hydrogen abstraction, this seems to be improbable with the present state of knowledge.

#### Hydrogen abstraction by *tert*-butoxyl radicals from toluenes

As in the case of *tert*-butoxyl radicals, a simple linear equation yields a satisfactory description. Again, the three-radical scales ( $\sigma_{\text{C}}^+$ ,  $\sigma_{\text{I}}^+$ ,  $\sigma_{\text{R}}^+$ ) are exceptions. For *para* substituents the Fisher–Meierhofer or Dresheim scale seems to be the best variable, and for the entire set  $\sigma^+$  is superior;

$$\log k_3(30^\circ\text{C}) = -1.470 - 0.586\sigma^+ \quad (11)$$

$n = 13; R = 0.9372; F = 79.46;$   
 $p < 0.00043\%; s = 0.110$

The Hammett  $\sigma$  is slightly more inaccurate and factored sigmas are even worse, but still significant:

$$\log k_3(30^\circ\text{C}) = -1.453 - 0.642\sigma_{\text{I}} - 0.694\sigma_{\text{R}} \quad (12)$$

$n = 14; R = 0.8406; F = 13.24;$   
 $p < 0.18\%; s = 0.191$

Of the bilinear equations, the stepwise linear regression algorithm has selected

$$\log k_3(30^\circ\text{C}) = -1.410 - 0.810\sigma + 0.337\sigma_{\text{C}}^+ \quad (13)$$

$n = 12; R = 0.9628; F = 57.19;$   
 $p < 0.0017\%; s = 0.0873$

as the most appropriate, which is recommended for prediction purposes. Figure 3 shows the scatter of measured and calculated rate constants. The negative regression coefficients suggest an electrophilic mechanism. The absolute values of these coefficients are similar to those of *tert*-butoxyl radical, not showing significantly more expressed electrophilic character. This is in sharp contrast to the observations of the hydrogen abstraction reactions from phenols, for which large negative reaction constants ( $\rho$ ) have indicated a definitely polar transition state. If this similarity is not radical but substrate specific, large negative reaction constants can be predicted for *tert*-butoxyl + phenol reactions.

$\sigma_{\text{FM}}^+$  (or  $\sigma_{\text{D}}^+$ ) never appears as a second variable in the equations but always alone as an alternative to polar scales. Consequently, these scales carry the same information as does  $\sigma$  or  $\sigma^+$ , despite their definition. In fact,  $\sigma^+$  and  $\sigma_{\text{FM}}^+$  scales correlate well ( $R = 0.925$ ,  $n = 8$ ) with each other.

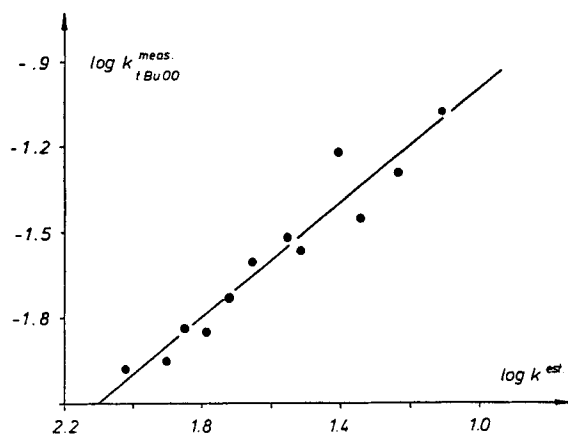


Figure 3. Measured (evaluated) vs calculated [by equation (13)] rate constants for hydrogen abstraction by *tert*-butylperoxyl radicals from substituted toluenes at 303 K

The general nature of these statements can be seen in a comprehensive study on the reaction



(here no distinction was made among peroxy radicals and the effect of the *o*-di-*tert*-butyl group was neglected on the basis of earlier results<sup>21</sup>). For hydrogen abstractions from phenols by peroxy radicals similar conclusions can be drawn as for that from toluenes. Fisher–Meierhofer and Dresheim scales or for the overall set  $\sigma^+$  have to be used to achieve a better description. Factored sigmas are poorer, but still significant. Of the radical scales, however,  $\sigma_\alpha$  seems to be more suitable than  $\sigma_c$ , but its involvement in the model is significant at a 29% level only. Nevertheless, the degrees of freedom were appreciably smaller ( $n = 5\text{--}12$ ) in the case of hydrogen abstraction reactions by phenols.

#### Evaluation of scales for radical reactions

Perhaps the most important conclusion is that there is no 'universal' radical scale even for a definite class of reactions, such as hydrogen transfer. The best possible scale should be determined separately, e.g. for each radical (type) and each substrate class. For *tert*-butyl radical inductive sigma ( $\sigma_I$ ) whereas for oxygen-centred radicals the Brown–Okamoto ( $\sigma^+$ ) scale is an acceptable choice. Radical sigma ( $\sigma^\cdot$ ) scales alone and in any self-combination are poor, except for the Fisher–Meierhofer and Dresheim scales, which are statistically indistinguishable from one another and carry similar information to 'polar' ionic sigmas. Considering the availability of  $\sigma_{\text{FM}}$  or  $\sigma_{\text{D}}$  compared with  $\sigma$  or  $\sigma^+$ , the use of the former radical scales should be avoided.

The Agirbas–Dinctürk–Jackson–Towson ( $\sigma_j$ )<sup>18</sup> scale is similarly inappropriate. It is not only the small number of substituents that limits its use but also experience. In the present work  $\sigma_j$  does not appear in descriptive equations even as a second variable, hence it cannot express the radical stabilization in hydrogen abstraction reactions properly. It is possible, however, that the  $\sigma_j$  obtained from kinetic data on substituted dibenzylmercury compounds<sup>18</sup> will give a good description for other reaction classes (e.g. decomposition, bond cleavage, isomerization, addition). The useful radical scales,  $\sigma_\alpha$  and preferably  $\sigma_c$ , have minor importance; the radical stabilization effect, if any, contributes at most 20–30% to the whole issue. Polar effects are much more important, not to mention the strength of the breaking bond. These radical sigmas as second variables in the model can successfully improve the fit. For the nucleophilic *tert*-butyl radical, the inductive effect measured by  $\sigma_I$  is of crucial importance and for oxygen-centred radicals primarily polar factors determine the rate constant.

Factored sigmas ( $\sigma_I, \sigma_R, \sigma_R^\ddagger$ ) are always among the acceptable representations, providing a deeper insight into the mechanism of a given process. The superiority of  $\sigma^+$  in every radical reaction (see Refs 9 and 15 in the Introduction) cannot be justified. Regarding the inter-laboratory reproducibility (e.g. Refs 12 and 23), the equations recommended predict the rate constants much better than the individual determinations.

#### CONCLUSIONS

In spite of the diverse data sets (originating from different laboratories) and assumptions used (e.g. solvent effects were neglected), significant correlations were obtained. The rates of hydrogen abstractions from substituted toluenes are determined by polar factors and radical stabilization plays only a minor role.

There is no general radical substituent scale ( $\sigma^\cdot$ ) for hydrogen abstraction reactions, either.  $\sigma_\alpha$  defined by Arnold and co-workers<sup>20</sup> and  $\sigma_c$  suggested by Creary and co-workers<sup>19</sup> can improve the description by ionic sigmas and indicate the role of radical stabilization. Other radical scales, however, are not recommended. Factored sigmas can be more suitable than unfactored ionic sigmas (e.g.  $\sigma_I$  for *tert*-butyl), but not necessarily. They give a more detailed insight into the mechanism, although they do not always achieve the best possible description.

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