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Steric and Electronic Substituent Effects in Tertiary Alkyl Peroxide Decompositions

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Abstract: Rate constants for the homolysis of aryl- substituted α-cumyl *tert*-butyl peroxides ($X\text{-}PhCMe_2OOCMe_3$) produce a Hammett plot with a ρ value of -0.22±.04. Both steric and electronic parameters influence the decomposition rate constants of tertiary alkyl peroxides with bulky substituents: $\log k_{rel} = (-0.40\pm 08)\Sigma\sigma^* - (0.43\pm .02)\Sigma E_s^c$.

It is generally assumed that the rates of thermal decompositions of alkyl peroxides are little influenced by electronic substituent effects.[1-3] For example, Richardson and co-workers using the Taft equation reported a relatively small ρ* value of -0.13 (chlorobenzene, 150 °C) for the decompositions of tertiary peroxides with electron withdrawing groups.[4] This small rate decelerating effect is consistent with the results from Hammett plots for decompositions of benzoyl peroxides (ρ = -0.38, dioxane, 80 °C),[5] *tert*-butyl peroxybenzoates (ρ = -0.38, carbon tetrachloride, 120 °C)[6] and *tert*-butyl phenylperacetates (ρ = -1.20, toluene, 56 °C, using σ^+).[7] We were therefore intrigued by the recent report of Matsuyama and Higuchi, who reported a very large electronic substituent effect for branched *tert*-alkyl *tert*-butyl peroxides.[8] A plot of $\log k_d$ at 150 °C vs. Σσ* for their data along with that of Richardson[4] yielded two straight lines of different slopes: a steep slope for peroxides with electron donating groups (ρ* = -11.0) and a small slope (ρ* = -0.13) for peroxides with electron withdrawing groups. The large acceleration effect was attributed to stabilization by a polar contribution to the activated complex which, presumably, is important only for peroxides with electron donating substituents.

In Matsuyama and Higuchi's work the electron donating substituents were branched alkyl groups which also might exert steric as well as electronic effects. Consequently, we have prepared and measured homolysis rate constants for a series of aryl-substituted α-cumyl *tert*-butyl peroxides, $X\text{-}PhCMe_2OOC(Me)_3$, in which X is H (**2a**), *p*-MeO (**2b**), *p*-Me (**2c**), *m*-MeO (**2d**), *p*-Cl (**2e**) and *p*-NO_2 (**2f**).[9-12] Differences in steric effects are minimal in this series and the electronic effects vary over one sigma unit. Our results along with those of Matsuyama and Higuchi are reported in Table I. The Hammett plot in Figure 1 gives a ρ value -0.22± .04 (r is 0.943). The peroxides with electron donating substituents show no excess rate acceleration.

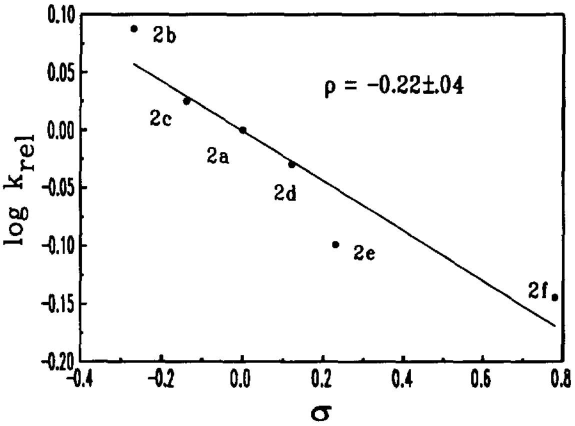

Figure 1. Hammett plot for decomposition of α-cumyl *tert*-butyl peroxides.

It appears that the rate acceleration observed for alkyl peroxides may be the result of increased steric repulsion incurred as the alkyl groups become more branched. Tidwell and co-workers found that *tert*-butyl 2,4,6-tri-*tert*-butyl peroxybenzoate decomposes 29 times faster than *tert*-butyl peroxybenzoate in cumene at 100 °C.[20] Recently, Taddei and co-workers, using molecular mechanics calculations, found that the bond dissociation energies of alkyl peroxides are generally similar, but substituent size may cause a decrease in the bond dissociation energy when a very bulky group such as 2,6-di-*tert*-butylcyclohexyl is present.[21] They suggest that steric factors may cause the small differences in bond dissociation energies, but conclude that polar effects may also be responsible for homolysis rate differences.

Table 1. Rate Constants for Decomposition of *tert*-Alkyl *tert*-Butyl Peroxides,$R(CH_3)_2COOC(CH_3)_3$

no.	R	k_d x10^5, s^{-1} [a]	$\Sigma\sigma^*$ [b]	ΣE_s^c [c]
2a	Ph	3.04[d]	-0.285	-5.04
2b	*p*-CH_3OPh	3.72[d]		
2c	*p*-CH_3Ph	3.22[d]		
2d	*m*-CH_3OPh	2.84[d]		
2e	*p*-ClPh	2.42[d]		
2f	*p*-NO_2Ph	2.20[d]		
3	Bis-$(CH_3)_3C$	48.4[d]	-0.730	-7.40
4a	$(CH_3)_3CCH_2$	6.70[e]	-0.644	-5.53
4b	$CH_3CH_2CH_2$	3.00[e]	-0.630	-4.64
4c	$(CH_3)_2CH$	4.30[e]	-0.625	-4.90
4d	CH_3CH_2	2.42[e]	-0.615	-4.45
4e	CH_3	1.6[f]	-0.600	-4.20
4f	$PhCH_2$	2.65[e]	-0.420	-4.65
4g	$ClCH_2$	1.63[e]	-0.115	-4.56

[a] Cumene, 125 °C. [b] Calculated by assuming inductive effects are additive so that σ^* for $R(CH_3)_2C$ is 2 times σ^* for CH_3CH_2 + σ^* for RCH_2(ref 8,17). [c] Calculated by eq 8, ref 18. [d] Calculated from unimolecular disappearance of 0.05 M peroxide monitored relative to an internal standard by GC. [e] Calculated using activation energies and k_d at 130 °C in ref 8. [f] Ref 19.

A comparison of the rate constant for **4a** to that of **4e** shows a four-fold rate increase when a methyl substituent is replaced by a neopentyl group.[8] In order to increase the acceleration effect, we prepared the highly substituted bis(1,1,2,2-tetramethylpropyl) peroxide (**3**) and found that it decomposes some thirty times faster than **4e** in cumene at 125 °C. A plot of $\Sigma\sigma^*$ vs. log (k_d/k_0), where k_0 is k_d for **4e**, is shown in Figure 2. The inclusion of the rate constant for **3** dramatically illustrates the non-linearity of the Taft equation plot. For the peroxides with $\Sigma\sigma^*$ greater than that of **4e**, the Taft equation plot (solid line, Figure 2) gives a ρ^* value of -11.3± 1.0 (r is 0.985). As seen by Matsuyama and Higuchi, the peroxides with benzyl and chloromethyl substituents appear to decompose much too rapidly. Our data for the phenyl substituted peroxide, **2a**, also appears to be fast. When the peroxides with weaker electron donating groups are included in the Taft equation calculation (dashed line, Figure 2), there appears to be no correlation: $\rho^* = -1.2 \pm 0.7$ (r is 0.535). In view of the small ρ value for the aryl substituted *α*-cumyl *tert*-butyl peroxides and the failure of electronic effects to fully account for all the peroxides in Figure 1, steric effects must considered .

Hancock constants (E_s^c), which correct for hyperconjugation contributions to E_s[22] may be calculated by a method developed by Fujita in which complex substituents are separated into component parts.[18] Using Fujita's method, we calculated Hancock constants for all of the peroxides in Figure 2. When **4e** is used as the standard, the plot of $\log(k_d/k_0)$ vs. ΣE_s^c as shown in Figure 3 gives a very good correlation with a slope of -0.46 ± 0.03 (r is 0.983). Included in this graph are the three peroxides which did not correlate with $\Sigma\sigma^*$. Steric effects are a major contributor to the rate acceleration for peroxides with branched alkyl substituents. However, as shown in Figure 1, electronic effects are not totally absent. Utilization of the Taft-Ingold equation (**eq 1**) which combines steric

$$\log k_{rel} = \rho^* \Sigma\sigma^* + \delta \Sigma E_s^c \qquad (1)$$

and electronic parameters[23,24] gives $\rho^* = -0.40 \pm 0.08$, $\delta = -0.43 \pm 0.02$, (r is 0.997) for peroxides **3**, **2a** and **4a-f**. Both ρ^* and δ are relatively small; the value of ρ^* is consistent with the value of -0.13 originally reported by Richardson.[4] It is evident that decomposition rates of tertiary alkyl peroxides are influenced by both steric and electronic effects.[25]

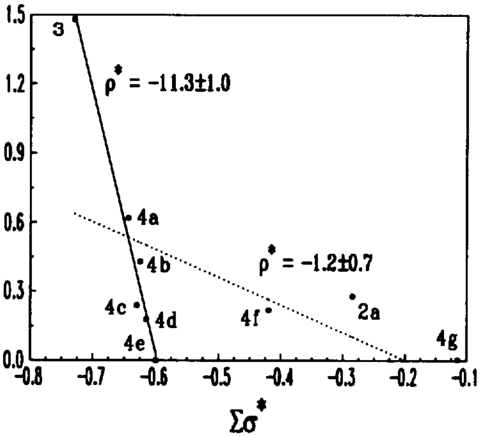

Figure 2. Electronic substituent effects on peroxide decomposition.

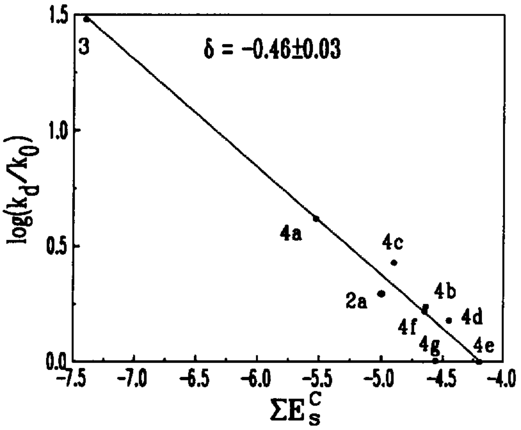

Figure 3. Steric substituent dffects on peroxide decomposition.

Acknowledgements.

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9. Peroxides **2a,c,d** and **e** were prepared by the addition of 20% excess anhydrous *tert*-butyl hydroperoxide in 2,2,3-trimethylpentane to a stirred H_2CCl_2 solution of the corresponding alcohol containing 10 mol% *p*-toluenesulfonic acid. **2a**, **2c** and **2e** were distilled at reduced pressure; **2a**: b.p 60°C (0.60 mmHg) (lit.[13] b.p 40°C , 0.4 mmHg), ^{1}H NMR: δ 7.12 (s, 6H), 1.56 (s, 6H) 1.12 (s, 9H)ppm; **2c**: b.p. 63°C(0.175 mmHg), ^{1}NMR: δ 7.17 (d, 2H, J = 8Hz), 6.92 (d, 2H, J = 8 Hz), 2.30 (s, 3H), 1.52 (s, 6H), 1.23 (s, 9H)ppm; **2e**: b.p. 52-55°C(0.10 mmHg), ^{1}NMR: δ 7.45 (m, 4H, 1.53 (s, 6H), 1.22 (s, 9H) ppm. **2d** was recrystallized from pentane at -78°C to give an oil: ^{1}NMR: δ 6.88 (m, 4H), 3.67 (s, 3H), 1.47 (s, 6H), 1.17 (s, 9H) ppm.
10. Peroxide **2b** was prepared as in note 9 with no catalysis. Column chromatography (florisil\pentane)yielded a clear liquid: ^{1}NMR δ 7.23 (d, 2H, J = 10Hz),3.67 (s, 3H), 1.47 (s, 6H), 1.17 (s, 9H) ppm.
11. Peroxide **2f** was prepared by the method of Kharash and Fono[14] by the copper (I) catalyzed decomposition of anydrous *tert*-butyl hydroperoxide in a benzene solution of *p*-nitrocumene. The crude peroxide was vacuum distilled at 0.5 mmHg and the third fraction (b.p. 118-119 °C) was chromatographed on silica gel (H_2CCl_2) to yield a clear oil : ^{1}NMR δ 8.17 (d, 2H J = 8Hz), 7.58 (d, 2H, J = 8Hz), 1.58 (s, 6H) ppm.
12. Peroxide **3** was made by the method of Davies [15] from the reaction of 1,1,2,2-tetramethyl hydroperoxide[16] with 2-bromo-2,3,3-trimethylbutane and silver trifluoroacetate. The crude product was distilled (b.p 38-41°C, 0.100 mmHg) and recrystallized from pentane at -78 °C to give a white solid (m.p. 28-28.5 °C: ^{1}NMR δ 1.18 (s, 2H), 0.93 (s, 3H) ppm .
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25. The steric effects result from repulsion of the alkyl groups and are not due to release of strain realized in a two-bond scission of the peroxide. If two bond-scission were occurring, then **4f** which would yield a benzyl radical should react faster than **4b** which would give a propyl radical.

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