multiuser computer which controls the experiment, averages the data from several laser shots, and processes the information.

**Irradiation and Product Analysis.** The irradiation of valerophenone and isovalerophenone was carried out in matched Pyrex tubes (9-mm o.d.) in a Rayonet reactor fitted with a merry-go-round and 14 RPR-3500 lamps. The concentrations of the ketones were in the 0.15–0.10 M range. The irradiated samples were analyzed for acetophenone by VPC on an Apiezon L column (5 ft) at 135 °C, using a Beckman GC-5 instrument equipped with flame ionization detectors.

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# Reaction of *tert*-Butoxy Radicals with Phenols. Comparison with the Reactions of Carbonyl Triplets

**P. K. Das, M. V. Encinas, S. Steenken, and J. C. Scaiano*[1]**

*Contribution from the Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556.* *Received November 12, 1980*

**Abstract:** *Tert*-butoxy radicals generated in the photodecomposition of di-*tert*-butyl peroxide react efficiently with phenols to yield the corresponding phenoxy radicals. Typical rate constants in benzene at 22 °C are $3.3 \times 10^8$ and $1.6 \times 10^9$ $M^{-1}$ $s^{-1}$ for phenol and *p*-methoxyphenol, respectively. The process is considerably slower in polar solvents; e.g., when pyridine is used as cosolvent, the rate constant for phenol drops to $4.7 \times 10^6$ $M^{-1}$ $s^{-1}$ as a result of strong hydrogen bonding which decreases the reactivity of the phenolic O–H group. Isotope effects (H/D) are typically in the 3–5 range.

The hydrogen abstraction reactions of alkoxy radicals have been a subject of considerable interest. Many extensive studies based on competition techniques by Walling,[3] Ingold,[4] Zavitsas,[5] and their co-workers have resulted in a vast amount of data regarding the relative rates of hydrogen abstraction reactions of *tert*-butoxy radical with various substrates. Recently, absolute rates of reactions of *tert*-butoxy radical with a large number of organic substrates[6-8] have been reported. Rate constants have been determined[6,7] by nanosecond laser flash photolysis by using di-*tert*-butyl peroxide as the photochemical source of *tert*-butoxy radicals and monitoring the formation of the ketyl radical resulting from hydrogen abstraction by *tert*-butoxy radical from diphenylmethanol (in competition with the reaction with another substrate).

In contrast to the numerous studies concerning the reactions of alkoxy radicals with various substrates including hydrocarbons, aldehydes, ethers, and alcohols, their reaction with phenols has drawn little attention. The kinetics and mechanisms of the reactions of *tert*-butoxy radical with phenols at 122 °C have been examined by Ingold[9,10] using competition techniques, but no absolute rates have been reported.

The similarity between the behavior of n,$\pi^*$ carbonyl triplets and alkoxy radicals toward hydrogen abstraction has been emphasized in several studies.[11-13] In addition to the similarity of the electronic configurations of n,$\pi^*$ triplets and alkoxy radicals, the thermochemistry of abstractions by both species is virtually identical, as a result of the close values of triplet excitation energies and double-bond contributions to the C=O bond.[14]

Table I. Kinetic Data for the Reactions of Para-Substituted Phenols with *tert*-Butoxy Radical and Spectral Data for Phenoxy Radicals in 1:2 Benzene–Di-*tert*-butyl Peroxide at 22 °C

| para substituent | $\lambda_{max}$,[a] nm | $\epsilon_{max}$[b] | highest concn,[c] mM | $k_3$,[d] $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| H | 400 | 0.64 | 42 | $3.3 \times 10^8$ |
| OH | 398 | 1.3 | 5 | $3.2 \times 10^9$ |
| $OC_2H_5$ | 404 | 1.4 | 21 | $1.7 \times 10^9$ |
| $OCH_3$ | 403 | 1.5 | 21 | $1.6 \times 10^9$ |
| $C(CH_3)_3$ | 404 | 1.0 | 31 | $5.6 \times 10^8$ |
| $C_2H_5$ | 404 | 0.91 | 33 | $5.3 \times 10^8$ |
| $CH_3$ | 404 | 0.91 | 17 | $5.5 \times 10^8$ |
| $C_6H_5$ | 502 | 0.80 | 33 | $5.3 \times 10^8$ |
| F | 392 | 0.54 | 40 | $3.8 \times 10^8$ |
| Cl | 412 | 0.86 | 29 | $2.9 \times 10^8$ |
| Br | 421 | 1.4 | 32 | $2.4 \times 10^8$ |
| I | 463 | 1.8 | 42 | $3.4 \times 10^8$ |
| CN | 443 | 0.51 | 22 | $9.7 \times 10^7$ |
| $NO_2$ | | | | $<1 \times 10^6$ |

[a] ±3 nm; this is the wavelength maximum in the spectral region, 355–650 nm. [b] ±20%; relative to $\epsilon_{max}$ of $Ph_2COH$, monitored at 545 nm. [c] This is the highest concentration of phenol used to measure $k_{exptl}$ (eq 4). [d] Estimated error, ±20%.

*tert*-butoxy radicals react with phenols producing phenoxy radicals which can be directly monitored by their spectral absorptions. In this paper, we report the results of an investigation of the kinetics of the hydrogen abstraction reactions from various phenols by *tert*-butoxy radical generated by laser photolysis. We also present a comparison between the behavior of carbonyl triplets and *tert*-butoxy radical as far as their hydrogen abstraction reactions with phenols are concerned.

## Results

**(a) Kinetics.** The photodecomposition of di-*tert*-butyl peroxide by pulses from a nitrogen laser (337.1 nm, 8 ns, ~3 mJ) was used as a source of *tert*-butoxy radical. In the presence of a hydrogen donor, e.g., phenol, the radical abstracts a hydrogen atom, a

(1) To whom correspondence should be addressed at the Division of Chemistry, National Research Council, Ottawa, Canada, K1A 0R6.

(2) The research described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is document No. NDRL-2145 from the Notre Dame Radiation Laboratory.

(3) Walling, C.; McGuiness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053–8 and references to earlier work therein.

(4) Ingold, K. U.; Carlsson, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 4891–4 and references to earlier work therein.

(5) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390–6 and references to earlier work therein.

(6) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 296–8. Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1978**, *100*, 4520–7.

(7) Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49–51.

(8) Wong, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 1235–9.

(9) Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2807–15.

(10) Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2816–25.

(11) Scaiano, J. C. *J. Photochem.* **1973**/1974, *2*, 81–118.

(12) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–177.

(13) Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 3361–4. Padwa, A. *Tetrahedron Lett.* **1964**, 3465–9.

(14) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1667–72, 1972–6.

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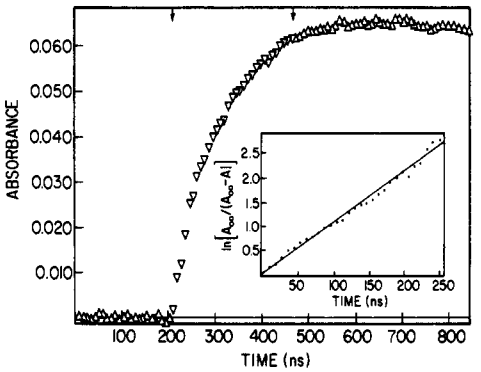


**Figure 1.** Experimental trace showing the formation of phenoxy radical monitored at 403 nm in 1:2 benzene–di-*tert*-butyl peroxide containing 0.03 M phenol and (insert) a plot of the data according to eq 5.

process that competes with the pseudo-first-order decay of *tert*-butoxy by either reaction with solvent or $\beta$ cleavage, i.e.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2\text{-}t\text{-BuO}\cdot \quad (1)$$

$$t\text{-BuO}\cdot \xrightarrow{k_2} \text{first-order decay} \quad (2)$$

$$t\text{-BuO}\cdot + \text{ArOH} \xrightarrow{k_3} \text{ArO}\cdot + t\text{-BuOH} \quad (3)$$

The details of the kinetic analysis have been reported elsewhere.[6,7] Phenoxy radicals usually have absorption bands in the 370–505-nm region (depending upon substitution) and are rather easy to monitor.[15-17] The buildup of the signal due to phenoxy radicals follows pseudo-first-order kinetics according to eq 4, where

$$k_{\text{exptl}} = k_2 + k_3[\text{ArOH}] \quad (4)$$

$k_{\text{exptl}}$ is the experimental pseudo-first-order rate constant derived from the experimental trace according to eq 5. $A_\infty$ and $A$ are

$$\ln\left(\frac{A_\infty}{A_\infty - A}\right) = k_{\text{exptl}}t \quad (5)$$

the transient optical absorptions in the plateau region and at time $t$, respectively. Figure 1 shows a typical trace, obtained in the case of phenol, and (insert) a plot of the data according to eq 5. The results were obtained in 1:2 benzene–di-*tert*-butyl peroxide (v/v) as solvent; this mixture has been shown to be a very convenient solvent for experiments of this type.[6,7]

Figure 2 shows representative plots according to eq 4 for hydroquinone, *p*-methoxyphenol, *p*-*tert*-butylphenol, *p*-fluorophenol, phenol, and *p*-cyanophenol. A summary of the data for all the phenols examined is given in Tables I and II. The intercept in Figure 2 corresponds to $k_2$, i.e., the reciprocal of the lifetime of *tert*-butoxy radicals in 1:2 benzene–di-*tert*-butyl peroxide; its value is in good agreement with that measured in the previous studies with diphenylmethanol[7] and triphenylphosphine.[19]

In some cases, e.g., *o*-methoxyphenol and *o*-fluorophenol, the determination of the rate constants by monitoring phenoxy radicals proved to be difficult because of low extinction coefficients of the phenoxy radicals. In such cases, the rate constants were measured by monitoring the formation of diphenylhydroxymethyl radical (at 545 nm) from diphenylmethanol (at constant concentration) in competition with the reactions with phenols (at varying concentration). The details of this method are given elsewhere.[6,7] That the method gives reliable rate constants for the reactions of *tert*-butoxy radical with phenols was checked by an experiment using *p*-bromophenol where the formations of both the *p*-bromophenoxy radical and the ketyl radical from diphenylmethanol were monitored at 425 and 545 nm, respectively. Experimental rate constants obtained by monitoring the two radicals agreed with one another within experimental error at every concentration of *p*-bromophenol, and their plots against *p*-bromophenol concentrations gave $k_3 = 2.1 \times 10^8$ $M^{-1}$ $s^{-1}$ which is practically the same as the rate constant ($2.4 \times 10^8$ $M^{-1}$ $s^{-1}$) obtained by using *p*-bromophenol alone.

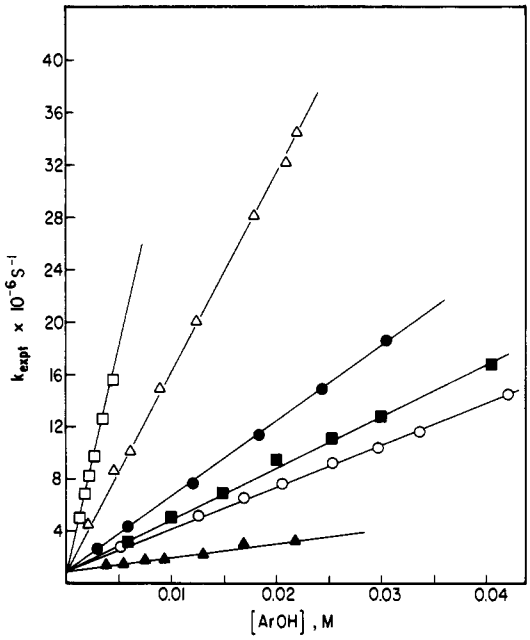


**Figure 2.** Plots of $k_{\text{exptl}}$ according to eq 4 for hydroquinone (□), *p*-methoxyphenol (△), *p*-*tert*-butylphenol (●), *p*-fluorophenol (■), phenol (○), and *p*-cyanophenol (▲).

Table II. Rate Constants for Hydrogen Abstraction by *tert*-Butoxy Radical from Various Phenols and Spectral Data for Phenoxy Radicals in 1:2 Benzene–Di-*tert*-butyl Peroxide at 22 °C[a]

| phenol | $\lambda_{max}$, nm | $\epsilon_{max}$ | highest concn, mM | $k$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| catechol | 383 | 0.46 | 6 | $1.7 \times 10^9$ |
| *o*-methoxyphenol | 375 | 0.16 | 35 | $1.7 \times 10^8$ |
| *o*-cresol | 377 | 0.46 | 42 | $5.4 \times 10^8$ |
| *o*-fluorophenol | 370 | 0.04 | 34 | $2.0 \times 10^8$ |
| *o*-bromophenol | 398 | 0.44 | 76 | $1.6 \times 10^8$ |
| *o*-cyanophenol | 403 | 0.36 | 20 | $1.7 \times 10^8$ |
| resorcinol | 403 | 0.56 | 9 | $8.9 \times 10^8$ |
| *m*-methoxyphenol | 408 | 0.51 | 17 | $4.0 \times 10^8$ |
| *m*-cresol | 407 | 0.66 | 22 | $3.8 \times 10^8$ |
| *m*-fluorophenol | 410 | 0.45 | 12 | $1.7 \times 10^8$ |
| *m*-bromophenol | 420 | 0.58 | 105 | $1.8 \times 10^8$ |
| *m*-cyanophenol | 413 | 0.36 | 31 | $1.0 \times 10^8$ |
| 2,6-di-*tert*-butylphenol | 378 | 0.38 | 38 | $4.3 \times 10^7$ |
| 2,6-di-*tert*-butyl-4-methylphenol | 380 | 0.52 | 20 | $1.2 \times 10^8$ |
| 2,4,6-trimethylphenol | 377 | 0.63 | 15 | $3.9 \times 10^9$ |
| 2,4,6-tribromophenol | 426 | 1.4 | 73 | $2.7 \times 10^8$ |
| 1-naphthol | 392 | 1.5 | 5 | $2.0 \times 10^9$ |
| 2-naphthol | 353 | 3.3 | 5 | $1.0 \times 10^9$ |

[a] Footnotes same as those in Table I.

No reaction leading to detectable transients was observed in the case of *p*-nitrophenol. In addition to the unreactivity of this molecule, the experiments were particularly difficult because of partial UV screening by the substrate.

**(b) Spectra.** The reactions of *tert*-butoxy radicals with phenols provided a relatively clean and convenient method of obtaining spectral data for the phenoxy radicals. Nearly all of the spectral data available for phenoxy radicals in the literature[15-18] were

(15) (a) Land, E. J.; Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1961**, *57*, 1885–93. (b) Land, E. J.; Porter, G. *Ibid.* **1963**, *59*, 2016–26. (c) Land, E. J.; Ebert, M. *Ibid.* **1967**, *63*, 1181–90.

(16) Habersbergerova, A.; Janovsky, I.; Teply, J. *Radiat. Res. Rev.* **1968**, *1*, 109–181. Habersbergerova, A.; Janovsky, I.; Kourim, P. *Radiat. Res. Rev.* **1972**, *4*, 123–31.

(17) Dobson, G.; Grossweiner, L. I. *Trans. Faraday Soc.*, **1965**, *61*, 708–14.

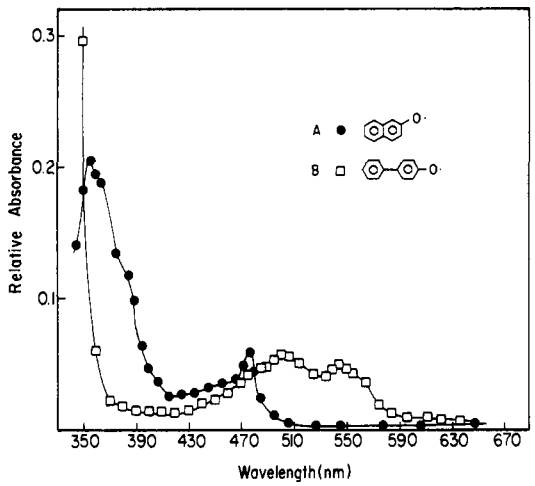


**Figure 3.** Spectra of 2-naphthoxy (●) and *p*-phenylphenoxy (□) radical in 1:2 benzene–di-*tert*-butyl peroxide.

Table III. Solvent, Temperature and Isotope Effects on the Rates of Hydrogen Abstraction by *tert*-Butoxy Radical from Phenol, *p*-Methoxyphenol, and *p*-Bromophenol

| solvent system[a] | temperature, °C | $k_3$, $M^{-1}$ $s^{-1}$ *p*-methoxyphenol | phenol | *p*-bromophenol |
|---|---|---|---|---|
| benzene | 22 | $1.8 \times 10^9$ | $3.3 \times 10^8$ | $3.4 \times 10^8$ |
| pyridine | 22 | $3.0 \times 10^7$ | $4.7 \times 10^6$ | $2.4 \times 10^6$ |
| *tert*-butyl alcohol | 22 | $9.3 \times 10^7$ | $1.5 \times 10^7$ | $7.7 \times 10^6$ |
| *tert*-butyl alcohol-$d_1$ | 22 | $2.6 \times 10^7$ | $3.1 \times 10^6$ | $1.9 \times 10^6$ |
| methanol | 22 | $1.1 \times 10^8$ | $2.2 \times 10^7$ | $1.8 \times 10^7$ |
| toluene | 22 | $1.6 \times 10^9$ | $3.3 \times 10^8$ | $3.0 \times 10^8$ |
| | 0 | $8.8 \times 10^8$ | $2.3 \times 10^8$ | $2.2 \times 10^8$ |
| | −15 | $6.4 \times 10^8$ | $1.8 \times 10^8$ | $1.6 \times 10^8$ |
| | −30 | $4.3 \times 10^8$ | $1.3 \times 10^8$ | $1.2 \times 10^8$ |
| | −45 | $2.2 \times 10^8$ | $8.7 \times 10^7$ | $6.8 \times 10^7$ |
| | −60 | $1.1 \times 10^8$ | $5.2 \times 10^7$ | $3.7 \times 10^7$ |

[a] In 1:1 (v/v) mixture with di-*tert*-butyl peroxide.

obtained by the methods of pulse radiolysis (in aqueous solution) or direct flash photolysis. Figure 3 shows two representative spectra obtained for 2-naphthol and *p*-phenylphenol. The absorption maxima of the phenoxy radicals in 1:2 benzene–di-*tert*-butyl peroxide (obtained by examining the spectral region, 350–650 nm) are given in Tables I and II. In many cases, the absorption maxima were found to be slightly blue-shifted relative to those reported in aqueous solution.[15-18]

The extinction coefficients of the phenoxy radicals at their wavelength maxima were determined relative to the extinction coefficient of the ketyl radical ($Ph_2COH$) from diphenylmethanol at 545 nm. Equation 6 was used for this purpose, where the

$$\frac{\epsilon_{ArO\cdot}}{\epsilon_{Ph_2\dot{C}OH}} = \frac{A_{ArO\cdot}}{A_{Ph_2\dot{C}OH}} \frac{k_{3P}[ArOH] + k_2}{k_{3P}[ArOH]} \frac{k_{3B}[Ph_2CHOH]}{k_{3B}[Ph_2CHOH] + k_2} \quad (6)$$

subscripts P and B refer to phenol and diphenylmethanol, respectively; *A*'s are the absorbances measured at the respective wavelength maxima, $k_3$'s are the rate constants for the hydrogen abstraction reactions (eq 3), and $k_2$ is the first-order decay constant for *t*-BuO· in 1:2 benzene–di-*tert*-butyl peroxide. The experiments were carried out in matched cells under such conditions that 70–90% of the reaction of *t*-BuO· led to hydrogen abstraction (eq 3) and the absorption due to the phenols at 337.1 nm (exciting laser wavelength) can be neglected.

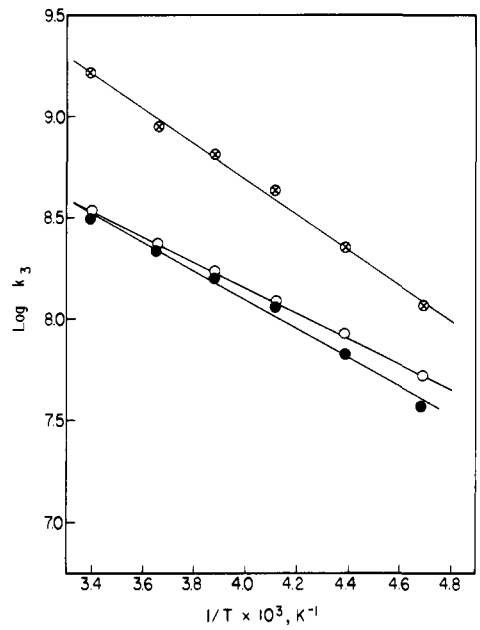


**Figure 4.** Arrhenius plots for reaction of *t*-BuO· with *p*-methoxyphenol (⊕), phenol (○), and *p*-bromophenol (●) in 1:1 toluene–di-*tert*-butyl peroxide.

Table IV. Activation Parameters for Hydrogen Abstraction by *tert*-Butoxy Radical from Phenol, *p*-Methoxyphenol, and *p*-Bromophenol in 1:1 Toluene–Di-*tert*-butyl Peroxide

| phenol | $E_a$[a] | log *A*, $M^{-1}$ $s^{-1}$ | $k_3$,[b] $M^{-1}$ $s^{-1}$ |
|---|---|---|---|
| *p*-methoxyphenol | 4.0 | 12.11 | $1.6 \times 10^9$ |
| phenol | 2.8 | 10.66 | $3.3 \times 10^8$ |
| *p*-bromophenol | 3.2 | 10.90 | $3.0 \times 10^8$ |

[a] In kcal $mol^{-1}$. [b] At 22 °C.

The relative extinction coefficients have been included in Tables I and II. Absolute values could be estimated by using the value for diphenylhydroxymethyl reported in the literature ($\epsilon_{max}$ = 3220 $M^{-1}$ $cm^{-1}$).[20] The errors of absolute values estimated in this manner may exceed 30%.

**(c) Solvent and Isotope Effects.** We have measured the rate constants for hydrogen abstraction by *t*-BuO· from a number of phenols in several solvent systems where benzene is replaced as cosolvent by polar and hydrogen-bonding solvents. The data are given in Table III. It is noted that the rates of hydrogen abstraction are considerably slower when benzene or toluene is substitution by pyridine or *tert*-butyl alcohol. The magnitude of the decrease in the rate constant on going from relative nonpolar to relatively polar hydrogen-bonding medium is in the order *p*-bromophenol > phenol > *p*-methoxyphenol.

Attempts to carry out some experiments in acetonitrile were unsuccessful, apparently as a result of a much higher value of $k_2$ resulting from a combination of more efficient $\beta$ cleavage and hydrogen abstraction from the solvent.[21]

When *tert*-butyl alcohol is replaced by *tert*-butyl alcohol-$d_1$, three- to fivefold decrease is noticed in the hydrogen abstraction rate constants (Table III). This is attributable to kinetic isotope effect because in *tert*-butyl alcohol-$d_1$, phenols are expected to be deuterated by reaction 7. Addition of 4% of $H_2O$ or $D_2O$ to

$$ArOH + t\text{-}BuOD \rightleftharpoons ArOD + t\text{-}BuOH \quad (7)$$

(18) (a) Schuler, R. H.; Buzzard, G. K. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 563–74. (b) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825–31.

(19) Griller, D.; Ingold, K. U.; Patterson, L. K.; Scaiano, J. C.; Small, R. D., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3780–5.

(20) Land, E. J. *Proc. R. Soc. London, Ser. A* **1968**, *305*, 457–71.

(21) In the presence of diphenylmethanol the formation of diphenylhydroxymethyl radicals is quite evident; however, the process is too slow and a study of the lifetime of the precursor rules out the possibility of a *t*-BuO· reaction. Most possibly the generation of $Ph_2\dot{C}OH$ is the result of the reactions of $CH_3\cdot$ and $\cdot CH_2CN$ radicals.

*t*-BuOH or *t*-BuOD, respectively, did not alter the isotope effect, indicating that the exchange was essentially quantitative.

**(d) Effect of Temperature.** The rate constants for hydrogen abstraction by *t*-BuO· from a number of phenols have been obtained in 1:1 toluene–di-*tert*-butyl peroxide at various temperatures in the range −60 to + 22 °C (Table III). As Figure 4 shows, the abstraction kinetics obeys Arrhenius equation reasonably well. The activation parameters are given in Table IV.

## Discussion

The present study reports for the first time absolute rate constants for hydrogen abstraction reactions of *tert*-butoxy radicals with phenols. One question that needs to be considered is whether the kinetic analysis in terms of formation of phenoxy radicals is valid in view of possible hydrogen abstraction reactions from phenols by radicals other than *tert*-butoxy. These radicals include methyl, formed through $\beta$ cleavage of *tert*-butoxy, and radicals such as $\cdot CH_2OH$, $C_6H_5CH_2\cdot$, and $(CH_3)_3COOC(CH_3)_2CH_2\cdot$, formed by hydrogen abstraction from solvents. A pulse radiolytic study[22] with $CH_3\cdot$ radical (generated from methyl chloride) has shown that the reactions of $CH_3\cdot$ with phenols in aqueous solution are slower than those of *tert*-butoxy in polar media by over 1 order of magnitude; the other solvent-derived radicals are expected to be even less reactive; for example, in experiments where both diphenylmethanol and a phenol were used as substrates competing for reaction with *tert*-butoxy, we did not observe any appreciable change in he decay rate of diphenylhydroxymethyl radical (relative to the systems where no phenol was used). This coupled with the fact that in nearly all of our experiments $k_3[\mathrm{ArOH}] > k_2$ establishes that the reactions from radicals other than *tert*-butoxy make only negligible contributions to the formation of phenoxy radicals.

The spectra of the phenoxy radicals we have obtained agree well with those available in the literature[15-18] after making allowance for slight solvent-induced shifts. This establishes the identity of the transient species monitored in our experiments. The effect of substitution on the absorption maxima of the phenoxy radicals is interesting (Tables II and III). While a substitution in the ortho position results in a blue shift of the absorption maximum, substitutions in the meta and para positions result in red shifts, in general. Although a trend in the absorption maxima moving to longer wavelengths is noticed with increasing Hammett $\sigma$ values of the substituents, there is no well-defined relationship.

The extinction coefficients which can be calculated on the basis of $\epsilon_{max} = 3220\ \mathrm{M^{-1}\ cm^{-1}}$ for diphenylhydroxymethyl are frequently in reasonable agreement with those available in the literature,[15] although in a few cases our values in benzene–di-*tert*-butyl peroxide are 20–40% lower than those reported. Whether this is the results of solvent effects or it merely reflects the uncertainty of the reference value for $\epsilon$ is not clear. The data in Tables I and II show that for a particular substituent $\epsilon_{max}$ follows the order para > meta > ortho. Relative to phenoxy radical, para substitution results in an increase in $\epsilon_{max}$ in most cases, while meta, and particularly ortho, substitution decreases $\epsilon_{max}$.

We shall now consider some mechanistic aspects of the hydrogen abstraction reactions of *tert*-butoxy with phenols. The large deuterium isotope effect, $k_{3H}/k_{3D} = 3.6$–$4.8$ in *tert*-butyl alcohol, clearly indicates that the breaking of the O–H bond is important in the transition state. As in the case of the reaction of triplet carbonyls, solvent effects do not reflect the importance of polar (or charge-transfer) configuration in the transition state. This effect is explainable primarily in terms of hydrogen bonding between the reactive site and the solvent molecules in polar solvents; this effect more than offsets any transition-state stabilization. That hydrogen bonding with reactants is important is also apparent from the observation tht the magnitude of the decrease in rate constants on going from relatively nonpolar to relatively polar solvents follows the order *p*-bromophenol > phenol > *p*-methoxyphenol. The strength of the hydrogen bond formed by the phenols follows the same order.

(22) Neta, P.; Steenken, S., unpublished work.

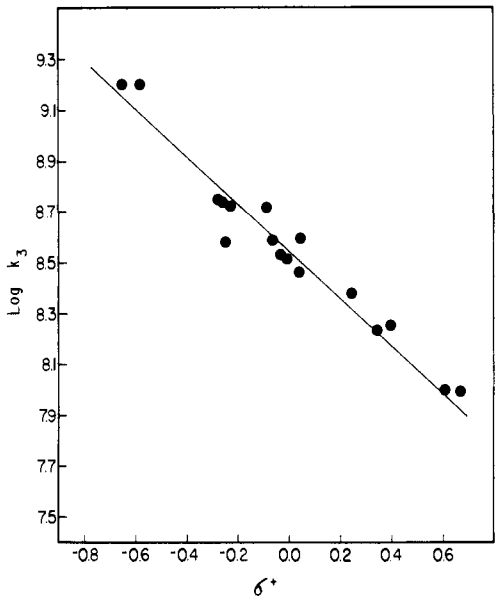


**Figure 5.** Hammett plot of the rate constants of reaction of *t*-BuO· with para- and meta-substituted phenols in 1:2 benzene–di-*tert*-butyl peroxide at 22 °C.

The absolute rate constants we have obtained for the hydrogen abstraction reactions by *tert*-butoxy from phenols are, in general, considerably larger than those obtained for the abstraction from other substrates such as hydrocarbons,[6] fatty acids,[7] and even amines.[23] While the O–H bond in phenol is rather weak ($D_{O\text{-}H} \approx 85$ kcal mol$^{-1}$),[24] it is comparable with some of the substrates that react far more slowly.[6] The high reactivity of phenols can be attributed to the low value of repulsive terms in atom transfers between oxygen centers.[25,26]

For a particular substituent, the rate constants for the reactions *t*-BuO· with substituted phenols follow the order para > ortho ≥ meta. The lower rate constants for the ortho-substituted phenols may be partly ascribed to steric effects. A Hammett plot using the rate constants for para- and meta-substituted phenols is shown in Figure 5. A value of −0.90 (at 22° C) is obtained for the reaction constant $\rho$. This is in good agreement with the value of −1.19 reported by Ingold[10] for the same reaction at 122 °C in carbon tetrachloride. The lower value in our study may be partly attributed to the aromatic nature of the solvent. The electronegative character of *t*-BuO· is believed[10] to be less in aromatic solvents because of a $\pi$-complex formation between the radical and aromatic $\pi$ electrons.

The "polar" or electrophilic character of *tert*-butoxy radicals has been a widely discussed topic in the literature[3-5,28-30] of hydrogen abstraction reactions of alkoxy radicals. On the basis of the relatively large values (−0.7 to −0.96) of the reaction constant

(23) Griller, D.; Howard, J. A.; Marriott, P.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619–623.

(24) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125–34. Cruickshank, F. R.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 1289–92. Benson, S. W. *J. Chem. Educ.* **1965**, 42, 502–518.

(25) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 934–8.

(26) In other words, for the transition-state configuration

the same factors which make the peroxide bond a weak one will make the repulsive term between the two oxygen end atoms a weak one.[25,27]

(27) Johnston, H. S. "Gas Phase Reaction Rate Theory"; Ronald Press: New York, 1966; Chapter 11.

(28) Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1963**, *85*, 2333–4; **1964**, *86*, 3369–3375.

(29) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108–12; Kennedy R.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 2381–5.

(30) Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc.* **1967**, *89*, 458–60.

($\rho$) and the fact that the correlation is better by using $\sigma^+$ values rather than $\sigma$ values, it has been suggested[29] that hydrogen abstraction by $t$-BuO· occurs through an electrophilic mechanism; i.e., partial charge separation takes place in the transition state. However, more recent studies[5,30] under conditions where complications due to chain reactions from chlorine atoms are eliminated gave much lower values for $\rho$ (−0.32 to −0.39) for the reactions of $t$-BuO· with para-substituted toluenes. It has been claimed[5] that $\rho$ reflects the differences in the bond dissociation energies of substituted toluenes (rather than the electrophilic nature of the abstraction mechanism) and that its magnitude is a measure of the sensitivity of the abstracting radical to these differences. Our data with substituted phenols clearly give a $\rho$ of significantly larger magnitude, and the plot of log $k_3$ against $\sigma^+$ gives a linear fit with better correlation than the plot of log $k_3$ against $\sigma$. This, coupled with the fact that phenol as a substrate is more susceptible to polar effects in the transition state than toluene, suggests that the reaction of $t$-BuO· with phenols would probably be best understood by an approach based on partial charge separation in the transition state (i.e., electrophilic mechanism).

We attempted to observe electron-transfer reaction, if any, between $t$-BuO· and $p$-dimethoxybenzene. The experiments were carried out in systems where benzene, *tert*-butyl alcohol, and a mixture (1:1) of *tert*-butyl alcohol and acetic acid were used as cosolvent with di-*tert*-butyl peroxide. There was no indication of the formation of cation of dimethoxybenzene in the spectral region 440–480 nm[31] nor was there any significant difference in the rate of formation of diphenylhydroxymethyl radical from diphenylmethanol in the presence and absence of $p$-dimethoxybenzene. Evidently, $t$-BuO· does not interact with $p$-dimethoxybenzene either by electron transfer or by any other mechanism (e.g., attack at the phenyl ring) under the conditions of our experiments.

In view of the fact[11-13] that carbonyl triplets present many similarities with $t$-BuO· in their hydrogen abstraction reactions, it is of interest to compare the kinetics of $t$-BuO· and benzophenone triplet in respect of their reactions with phenols. The data for benzophenone triplet are presented in the preceding paper. Both $t$-BuO· and benzophenone triplet appear to abstract hydrogen from phenols faster than from other substrates (e.g., hydrocarbons, alcohols, and ethers).[7,11] For a particular phenol, the rate constant for hydrogen abstraction by *tert*-butoxy radicals (in 1:2 benzene–di-*tert*-butyl peroxide) is smaller than the rate constant for the quenching of benzophenone triplets in benzene. The difference may reflect the increased importance of polar effects in the case of the benzophenone triplets while, in the case of *tert*-butoxy, the reactivity is largely (but not only?) controlled by the bond energy at the ArO–H site. While the Hammett $\rho$ values may not seem to favor this argument, we note that bond energies are somewhat sensitive to substituent effects and also that in the case of benzophenone, the faster reaction tends to decrease the sensitivity of the process to changes in the substrates.

It is clear that while in the case of *tert*-butoxy radicals the only reaction is hydrogen transfer, in the case of benzophenone triplets other interactions can also play a significant role; for example, the yields are low where a heavy atom is present in the substrate, as well as in experiments at low temperatures.[32] Thus, in terms of overall mechanism, the case of benzophenone triplets appears to be more involved than the case of *tert*-butoxy radicals, although the initial interactions of the two systems may be similar. While solvent and Arrhenius parameters for benzophenone triplets and *tert*-butoxy radicals are similar, isotope effects are substantially smaller in the case of benzophenone. This may be directly connected to the increase in rate constants. The behavior of $p$-methoxypropiophenone triplets shows high isotope effects; this is surprising in view of the fact that $\pi,\pi^*$ triplets do not usually show radical-like properties.

## Experimental Section

Di-*tert*-butyl peroxide was obtained from MC & B; it was distilled and treated in an alumina column before use. Samples prepd. from di-*tert*-butyl peroxide that was only passed through alumina (with no prior distillation) gave essentially the same results. The source and purification of phenols and other chemicals are described in the preceding paper.[32] Diphenylmethanol (MC & B) was sublimed twice before use.

The details of the laser photolysis setup are also given in the preceding paper.[32] All the samples were deaerated by passing oxygen-free argon. In the experiments where the ratio of di-*tert*-butyl peroxide and cosolvent was 2:1, the laser output (~3 mJ) was attenuated to about half its original value by using neutral density filters in order to avoid second-order contributions to the decay of *tert*-butoxy radicals.

(31) The cation of $p$-dimethoxybenzene has on absorption maximum at 460 nm, as shown by pulse radiolytic studies in aqueous solution; O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773–9.

(32) Das, P. K.; Encinas, M. V.; Scaiano, J. C., preceding paper in this issue.

# Reactions of Coordinated Molecules. 30. Carbon–Carbon Bond Formation between Adjacent Acyl Ligands: Transannular Coupling across a Metalla-$\beta$-diketonate Ring

**C. M. Lukehart* and K. Srinivasan**

*Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.* *Received January 19, 1981*

**Abstract:** When the metalla-$\beta$-diketonate complex $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$ is treated with a stoichiometric amount of KH, a proton of the acetyl group is removed, affording an anionic complex in essentially quantitative yield with the molecular formula $\{[\eta\text{-}C_5H_5(OC)Fe(CH_2CO)(i\text{-}C_3H_7CO)]BF_2\}^-$. An X-ray structure of the $Me_4N^+$ salt of this complex is reported: $P2_1/c$ with $a$ = 9.640 (5) Å, $b$ = 14.687 (3), $c$ = 13.277 (3) Å, $\beta$ = 90.24 (3)°, $V$ = 1880 Å$^3$, and $Z$ = 4. The molecular structure reveals C–C bond formation between the original acyl carbon atoms. These two carbon atoms and the exomethylene carbon atom adopt an $\eta$-allyl coordination to the $\eta$-$C_5H_5(OC)Fe$ moiety. This interligand C–C bond formation represents a transannular coupling across the six-membered metalla-$\beta$-diketonate ring. The significance of this result pertaining to stoichiometric and catalytic reaction chemistry at metal atoms is discussed.

We reported recently the synthesis of several (metalla-$\beta$-diketonato) BXY complexes,[1,2] and an X-ray structure of one such ferra complex, $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$, **1**.[3] In complex **1**, the boron atom acts as a central coordinating atom

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