

## Generation and Reactivity toward Oxygen of Carbon-Centered Radicals Containing Indane, Indene, and Fluorenyl Moieties

Enrique Font-Sanchis, Carolina Aliaga, Elena V. Bejan, Raecca Cornejo, and J. C. Scaiano\*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

tito@photo.chem.uottawa.ca

Received November 5, 2002

Resonance-stabilized radicals containing indane, indene, and fluorenyl moieties exhibit attenuated reactivity toward oxygen. Rate constants of  $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$  were observed for the most stabilized radicals. The dependence of  $k_{\text{ox}}$  (rate constant for radical trapping by oxygen) on the corresponding bond dissociation energies revealed that stereoelectronic effects are more important than steric effects in determining the low radical reactivity with oxygen. Scavenging by the nitroxide TEMPO was also examined, and revealed that in this case steric effects are more important than in the case of oxygen. The rate constants for the hydrogen abstraction by cumyloxyl and *tert*-butoxyl radicals generated thermally and photochemically have been determined in benzene, and were in the range of ca.  $(1-13) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , showing that benzylic stabilization has a modest effect on substrate reactivity as a hydrogen donor toward alkoxy radicals.

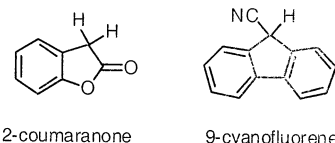
### Introduction

Since Gomberg prepared the persistent and stabilized triphenylmethyl radical in 1900 diverse examples of stabilized carbon-centered radicals have been reported.<sup>1-4</sup> Thus, it is known that the introduction of bulky substituents increases the persistency of the radicals; for example, perchlorotriphenylmethyl and perchloro-9-phenylfluorenyl radicals are rather persistent and unreactive toward oxygen in solid form.<sup>5,6</sup> However, the reaction of triphenylmethyl radicals with oxygen has been found to be reversible and, at room temperature and under air the equilibrium, is largely displaced toward the peroxy radical form.<sup>7,8</sup> Further, cyanobis(pentachlorophenyl)methyl and  $\alpha$ -isopropoxycarbonylbis(pentamethylphenyl)methyl radicals, the substituted analogues of the diphenylmethyl radical, are persistent and do not react with oxygen. The persistency of these radicals has been ascribed mainly to steric factors, rather than electronic effects.<sup>9</sup>

We use the term *persistent* as defined by Griller and Ingold to describe radicals that have "a lifetime significantly greater than methyl under the same conditions", while the term *stabilized* is reserved for radicals "when

the R-H bond strength is less than the appropriate C-H bond strength in an alkane".<sup>10</sup>

We have recently reported on the importance of electronic effects to explain the low reactivity with oxygen of some lactone and nitrile-derived carbon-centered radicals (oxygen quenching rate constants  $\leq 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>11-13</sup> Further, the reactivity enhancement for the hydrogen abstraction from these compounds with *tert*-butoxyl radicals (especially 2-coumaranone and 9-cyano-fluorene) has showed the stabilizing effect of the lactone and cyano group on the radical generated.

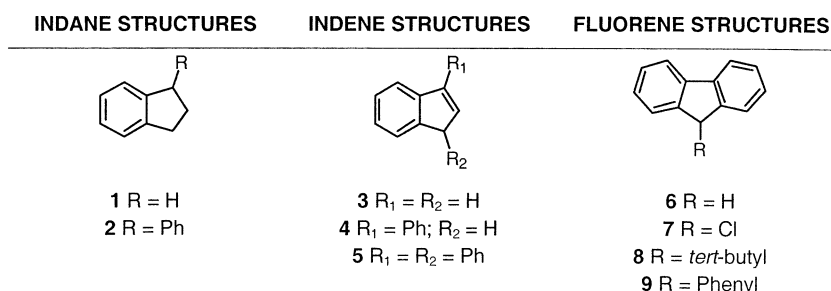


We have proposed five parameters to explain the diminished reactivity toward oxygen of carbon-centered radicals: (a) benzylic resonance stabilization; (b) favorable stereoelectronic effects; (c) unpaired spin delocalization on heteroatoms, particularly oxygen; (d) electron-withdrawing effects; and (e) steric effects.<sup>12</sup> Thus, the present studies were undertaken in an attempt to understand better the structural parameters that can attenuate the reactivity of carbon-centered radicals with molecular oxygen, and to test the validity of the paradigm of points a-e for a group of structurally related hydrocarbon radicals.

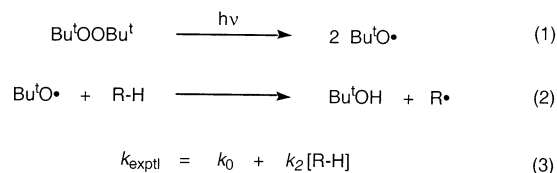
(1) Gomberg, M. J. *J. Am. Chem. Soc.* **1900**, *22*, 757-771.  
 (2) Koelsch, C. F. *J. Am. Chem. Soc.* **1957**, *79*, 4439-4441.  
 (3) Ziegler, K.; Ochs, C. *Chem. Ber.* **1922**, *55*, 2257-2277.  
 (4) Sabacky, M. J.; Johnson, C. S.; Smith, R. G.; Gutowsky, H. S.; Martin, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2054-2058.  
 (5) Ballester, M.; Riera-Figueras, J.; Castaner, J.; Badia, C.; Monso, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215-2225.  
 (6) Ballester, M.; Castaner, J.; Pujadas, J. *Tetrahedron Lett.* **1971**, *20*, 1699-1702.  
 (7) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1968**, *46*, 2655-2660.  
 (8) Janzen, E. G.; Johnston, F. J.; Ayers, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 1176-1183.  
 (9) Clarke, L. F.; Hegarty, A. F.; O'Neill, P. *J. Org. Chem.* **1992**, *57*, 362-366.

(10) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13-19.  
 (11) Scaiano, J. C.; Martin, A.; Yap, G. P. A.; Ingold, K. U. *Org. Lett.* **2000**, *2*, 899-901.  
 (12) Bejan, E. V.; Font-Sanchis, E.; Scaiano, J. C. *Org. Lett.* **2001**, *3*, 4059-4062.  
 (13) Font-Sanchis, E.; Aliaga, C.; Focsaneanu, K.-S.; Scaiano, J. C. *Chem. Commun.* **2002**, *15*, 1576-1577.

## CHART 1



## SCHEME 1



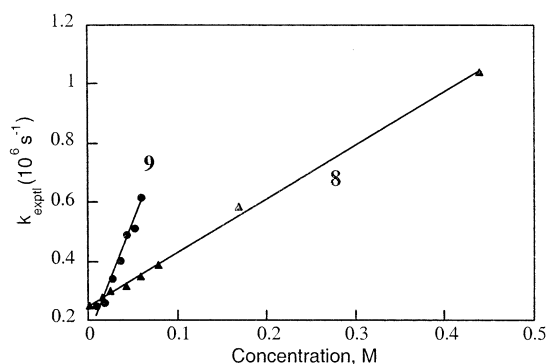
In this context, we now report the generation and reactivity with oxygen of radicals derived from the aromatic compounds in Chart 1. We chose these molecules to establish the importance of resonance stabilization and steric effects to explain the unreactivity of certain carbon-centered radicals with oxygen. As part of this work, we have also examined the reactivity of these substrates toward alkoxy radicals.

## Results

**Hydrogen Donor Ability.** The reactivity of compounds **2**, **4**, **6**, **8**, and **9** toward alkoxy radicals was determined by studying their reaction with *tert*-butoxyl radicals with use of laser flash photolysis techniques.<sup>14</sup> The radicals produced in these reactions have convenient absorptions that can be used to monitor directly their formation.

Thus, *tert*-butoxyl radicals were produced by 355-nm laser excitation of a deaerated solution of the peroxide in benzene 50% (v/v) (reaction 1, Scheme 1). The growth of the radical signal reflects reaction 2 ( $k_2$ ) and includes any other form of reaction between *tert*-butoxyl and RH (even when the product is undetectable). The term  $k_0$  incorporates other forms of decay of *tert*-butoxyl that do not depend on substrate concentration, such as reaction with the solvent and  $\beta$ -cleavage. The experimental rate constant for the growth is given by eq 3. Figure 1 shows two representative plots according to eq 3 from which the values of  $k_2$  are obtained. The rate constants determined are given in Table 1.

Unfortunately, radicals formed from **1** and **3** did not produce good signals that could be used to monitor their formation at different concentrations of substrate. Moreover, **5** absorbs at 355 nm, so it was impossible to calculate  $k_2$  for this compound with this method. These problems led us to use another method. Thus, thermolysis of di- $\alpha$ -cumyl hyponitrite has been used to calculate the reactivity of cumyloxy radicals toward hydrocarbons



**FIGURE 1.** Determination of the rate constant for the reaction of *tert*-butoxyl radicals with 9-phenylfluorene (**9**) and 9-*tert*-butylfluorene (**8**) in benzene at room temperature.

**TABLE 1.** Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Substrates at Room Temperature in Benzene

substrate	concn of substrates, M	rate constant, <sup>a</sup> 10 <sup>6</sup> M <sup>-1</sup> s <sup>-1</sup>	monitoring wavelength, nm
diphenylmethane <sup>15</sup>		0.91	
<b>2</b>	0.03–0.06	8.1	340
<b>4</b>	0.02–0.14	<5.8 <sup>b</sup>	340
<b>6</b>	0.01–0.04	6.2	500
<b>8</b>	0.01–0.44	1.8	490
<b>9</b>	0.01–0.06	9.9	340

<sup>a</sup> Errors for rate constants were determined to be less than 5%.

<sup>b</sup> This value may incorporate some double bond addition that cannot be readily separated with laser photolysis techniques.

(Scheme 2).<sup>16</sup> In eq 7,  $k_a$  is the rate constant for the hydrogen atom abstraction,  $k_\beta$  is the rate constant for the  $\beta$  scission, and  $k_0'$  incorporates the hydrogen atom abstraction from the solvent and from dicumyl hyponitrite.

This method was used to determine  $k_a$  for **1**, **3**, and **5**. Thermolysis of dicumyl hyponitrite (0.0027 M) was carried out in deaerated benzene at 30 °C for 12 h in the presence of various substrate concentrations (0–70 mM). The relative yields of 2-phenyl-2-propanol (A) and acetophenone (K) were determined by gas chromatography. The plot of A/K vs [RH] yields  $k_a/k_\beta$  from the slope, where the contribution of  $k_0'$  has been neglected in eq 7.

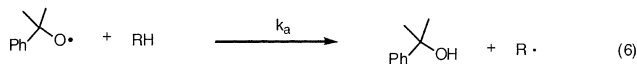
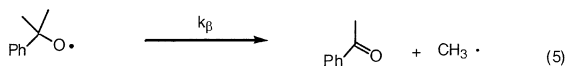
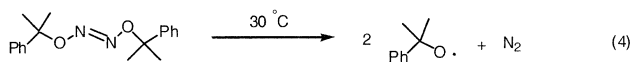
The values of  $k_a$  for **1**, **3**, and **5** (see Table 2) were obtained by using  $k_a$  determined for Ciba Irganox HP-

(14) Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(15) Arends, I. W. C. E.; Mulder, P.; Clark, K. B.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8182–8189.

(16) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Luszytyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466–470.

## SCHEME 2



$$\frac{[A]}{[K]} = \frac{k_a}{k_\beta} [\text{RH}] \quad (7)$$

$$\frac{\text{slope for RH}}{\text{slope for HP-136}} = \frac{k_a}{k_\beta} \frac{k_a^{\text{HP-136}}}{k_\beta^{\text{HP-136}}} \quad (8)$$

**TABLE 2. Rate Constants for the Reaction of Cumyloxyl Radicals with Substrates at 30 °C in Benzene**

substrate	rate constant, <sup>a</sup> 10 <sup>6</sup> M <sup>-1</sup> s <sup>-1</sup>
Ciba Irganox HP-136	12.4 <sup>b</sup>
<b>1</b>	5.40
<b>3</b>	6.80
<b>5</b>	13.0

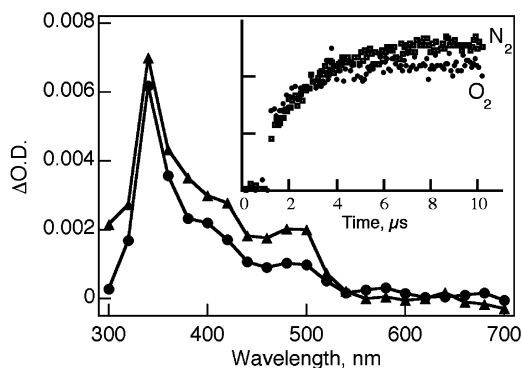
<sup>a</sup> Errors for rate constants are estimated at 10%. <sup>b</sup> Calculated by laser flash photolysis of dicumyl peroxide in the presence of different amounts of HP-136 in benzene at room temperature.

136<sup>11</sup> ( $k_a^{\text{HP-136}}$ ), using the first method (see eqs 1–3) and dicumyl peroxide as source of cumyloxyl radicals (see eq 8).

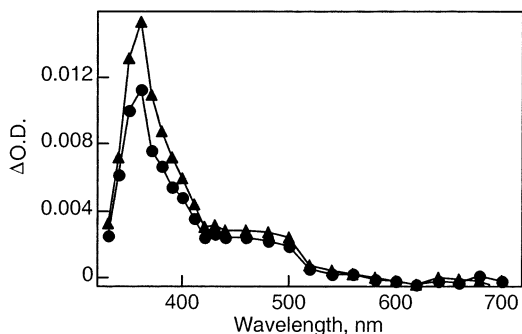
In general, the rate constants were not unusual for benzylic C–H bonds. Higher rate constants were observed for those compounds that generated more resonance-stabilized radicals.

**Reactivity toward Oxygen.** The first two molecules chosen for study, indane (**1**) and 1-phenylindane (**2**), present only benzylic resonance stabilization. Photolysis of di-*tert*-butyl peroxide in the presence of **2** shows the formation of a radical, where the UV band, centered around 340 nm, is virtually identical with that for the diphenylmethyl radical.<sup>17</sup> In an oxygen-saturated sample, the signal for radical **2** was completely suppressed. The same high reactivity toward oxygen was observed for the radical from indane **1**.

The study of the second series of molecules based on the indene structure (**3–5**) should reveal the importance of the stereoelectronic effects due to the presence of the indene ring and also phenyl substituents. Photolysis of di-*tert*-butyl peroxide in the presence of 3-phenyl-1-indene (**4**) yielded a transient with an absorption band at 340 nm together with weak signals at 420 and 500 nm. Similar experiments under oxygen (Figure 2) produced the same spectra but with a diminished band at 340 nm. Monitoring at 340 and 420 nm, the comparison of nitrogen- and oxygen-saturated samples showed that oxygen only affected the signal at 340 nm, indicating that two different radicals were generated. It has been previously reported that *tert*-butoxyl radicals react with indene



**FIGURE 2.** Transient absorption spectra recorded following 355-nm laser excitation of a sample containing 10.4 mM 3-phenyl-1-indene (**4**) in benzene/di-*tert*-butyl peroxide (50/50) under oxygen, (●) 0.72 and (▲) 10.1 μs after the laser pulse. Inset: Transient kinetic traces recorded at 420 nm under nitrogen (□) and oxygen (○).

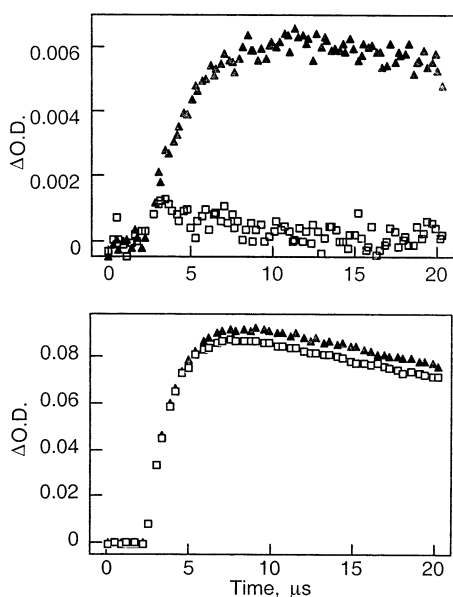


**FIGURE 3.** Transient absorption spectra recorded following 355-nm laser excitation of a sample containing 4 mM 1,3-diphenyl-1-indene (**5**) in benzene/di-*tert*-butyl peroxide (50/50) under nitrogen, (●) 5.28 and (▲) 9.52 μs after the laser pulse.

by hydrogen abstraction at the allylic position and addition to the double bond.<sup>15</sup> Addition to the double bond is expected to occur at the 2-position in **4**, and addition to the 1-position is less likely and results in the formation of a secondary alkyl radical, which is not detectable in the UV–visible region. Thus, the transient at 340 nm, which was quenched by oxygen, could be assigned to the 1-phenyl-2-*tert*-butoxyindanyl radical; and the absorption bands at 340, 420, and 500 nm that were not affected by oxygen are assigned to the 1-phenylindanyl radical. Note that rate determinations with laser flash photolysis techniques include all modes and sites of reaction, regardless of which species is monitored.

The radical generated from laser flash photolysis of di-*tert*-butyl peroxide in the presence of indene **3** was readily quenched by oxygen, as expected. Finally, the laser flash photolysis of di-*tert*-butyl peroxide in the presence of 1,3-diphenyl-1-indene (**5**) yielded a transient with absorption bands at 360 and 500 nm (Figure 3); this transient could be ascribed to the 1,3-diphenylindanyl radical. The same spectrum was obtained when the experiment was carried out under an oxygen atmosphere; moreover, the growth at 360 nm was only slightly affected by oxygen. No benzylic product-radical arising from addition to the double bond was generated in this case. Steric effects due to the presence of a second aromatic ring in the indene

(17) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396–4403.



**FIGURE 4.** Top: Transient kinetic traces recorded at 500 nm following 355-nm laser excitation of a sample containing 0.134 M fluorene **6** in benzene/*di-tert*-butyl peroxide (50/50). Bottom: Transient kinetic traces recorded at 340 nm following 355-nm laser excitation of a sample containing 0.067 M 9-phenylfluorene (**9**) in benzene/*di-tert*-butyl peroxide (50/50). Traces in both panels recorded under nitrogen (▲) and oxygen (□).

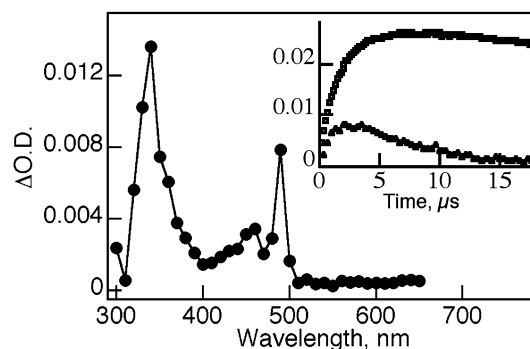
structure might explain the absence of addition at the alkene moiety.

Clearly, the planarity of the radical caused by the five-member ring, while important, is not sufficient to induce lack of reactivity toward oxygen, and the  $\pi$ -stabilization of the phenyl substituent at the benzylic position is an important factor.

In the third series of selected molecules, containing the five-member ring of fluorene and substituted at the 9-position provides benzylic resonance stabilization, favorable stereoelectronic effects, and in most cases significant steric hindrance at the radical center.

The photolysis of *di-tert*-butyl peroxide in the presence of fluorene **6** shows the formation of the fluorenyl radical whose spectra has already been reported,<sup>18</sup> with a sharp maximum around 500 nm. Comparing the laser photolysis results for nitrogen- and oxygen-saturated samples, we observed that, not surprisingly, the signal for the fluorenyl radical was totally suppressed (Figure 4, top). Employing 9-chlorofluorene (**7**) as a photochemical source of the fluorenyl radical, the high reactivity toward oxygen was confirmed. Part of the motivation to study **7** is related to the determination of the rate constant for the reaction of the radical with oxygen, *vide infra*.

Two other molecules based on the fluorene moiety were also examined, 9-phenylfluorene (**9**) and 9-*tert*-butylfluorene (**8**). The photolysis of *di-tert*-butyl peroxide in the presence of 9-phenylfluorene shows that the growth at 340 nm due to the 9-phenylfluorenyl radical is unaffected by oxygen (Figure 4, bottom).<sup>19</sup> To know if  $\pi$ -sta-



**FIGURE 5.** Transient absorption spectra recorded following 355-nm laser excitation of a sample containing 0.5 M 9-*tert*-butylfluorene (**8**) in benzene/*di-tert*-butyl peroxide (50/50) under nitrogen 0.8  $\mu$ s after the laser pulse. Inset: Transient kinetic traces recorded at 490 nm under nitrogen (□) and oxygen (▲).

**TABLE 3.** Rate Constants for the Reaction of Oxygen with the Radicals Generated from Different Substrates at Room Temperature<sup>a</sup>

radicals from <sup>b</sup>	rate constant, $10^5 \text{ M}^{-1} \text{ s}^{-1}$	monitoring wavelength, nm
diphenylmethane <sup>17</sup>	6300	
<b>4</b>	8.2	500
<b>5</b>	2.8	380
<b>7</b> <sup>c</sup> (same radical as <b>6</b> )	920	500
<b>8</b>	166	490
<b>9</b>	7.6	340

<sup>a</sup> Rate constants were estimated by monitoring the decay of the radicals in nitrogen-, air-, and oxygen-saturated samples. Errors for rate constants were calculated to be less than 10%. <sup>b</sup> The radicals were generated from the corresponding compounds by laser excitation of *tert*-butyl peroxide in benzene, using 355-nm pulses. <sup>c</sup> Excitation at 266 nm was used for direct photolysis of haloalkane **7**, leading to the fluorenyl radical.

bilization of the phenyl substituent or steric effects are the major cause of the reduced reactivity toward the oxygen of radical **9**, the substrate 9-*tert*-butylfluorene (**8**) was studied. The photolysis of *di-tert*-butyl peroxide in the presence of **8** shows the formation of a transient with maxima at 340, 460, and 490 nm (Figure 5). This transient was assigned to the 9-*tert*-butylfluorenyl radical by comparison with the fluorenyl radical. Further, in an oxygen-saturated sample, the signal for radical **8** was totally quenched, with barely a fast spike indicating its presence in the early stages following the laser pulse. Thus, the failure to observe any reactivity of radical **9** toward oxygen, while radical **8** is reactive, suggests that the electronic effects due to the presence of the phenyl ring are more important in determining the lack of reactivity with oxygen. That is, **8** and **9** would not be expected to be that different if steric effects dominated.

To gather accurate data on the reactivity of these stabilized carbon-centered radicals with oxygen, the rate constants for reaction at room temperature were measured at different concentrations of oxygen, using laser flash photolysis (see Table 3). The rate constants for radicals derived from **4**, **5**, and **9** were at least ten thousand times slower than those for typical carbon-centered radicals. However, the presence of a bulky *tert*-butyl group at the 9-position of the fluorenyl ring only decreased the reactivity five times. On the other hand,

(18) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5934–5935.

(19) Siskos, M. G.; Zarkadis, A. K.; Steenzen, S.; Karakostas, N.; Garas, S. K. *J. Org. Chem.* **1998**, *63*, 3251–3259.

**TABLE 4. Rate Constants for the Reaction of Carbon-Centered Radicals with TEMPO**

radical from	rate constant, $10^5 \text{ M}^{-1} \text{ s}^{-1}$	monitoring wavelength, nm
Ciba Irganox HP-136 <sup>b</sup>	1.35	540
9-carbomethoxyfluorene	6.8	550
<b>1</b> <sup>a</sup>	2200	
<b>3</b> <sup>a</sup>	73	
<b>5</b> <sup>b</sup>	1.46	380
<b>6</b> <sup>a</sup>	310	
<b>8</b> <sup>b</sup>	<1	500
<b>9</b> <sup>b</sup>	<1	340

<sup>a</sup> See ref 15. <sup>b</sup> The radicals were generated from the corresponding compounds by laser excitation of *tert*-butyl peroxide in benzene, using 355-nm pulses.

we have reported that the oxygen quenching rate constant for the 9-carbomethoxyfluorenyl radical should be lower than  $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>13</sup> suggesting the importance of electronic effects in this system.

**Rate Constant for the Trapping of Carbon-Centered Radicals by TEMPO.** The reactions of carbon-centered radicals with nitroxides have been examined in considerable detail.<sup>20–22</sup> In general these reactions are quite fast, but below the diffusion-controlled limit. The rate constants for trapping are higher for aliphatic radicals, largely reflective of the reduced stabilization of these radicals. Thus, it seems interesting to investigate the reactions of some carbon-centered radicals toward 2,2,5,5-tetramethylpiperidin-1-oxyl (TEMPO). The rate constants were obtained from the transient decay at different TEMPO concentrations (see Table 4). Those radicals with extremely low reactivity toward oxygen (radicals generated from Ciba Irganox HP-136, 9-carbomethoxyfluorene, and 1,3-diphenylindene) showed the lowest rate constants. Interestingly, the 9-*tert*-butylfluorenyl radical and the 9-phenylfluorenyl radical were unreactive with TEMPO, even at TEMPO concentrations as high as 0.1 M. It is clear that steric effects due to the presence of the *tert*-butyl group in **8** are enough to control the lack of reactivity in the case of the hindered TEMPO radical. Naturally, radical **9** was also unreactive.

## Discussion

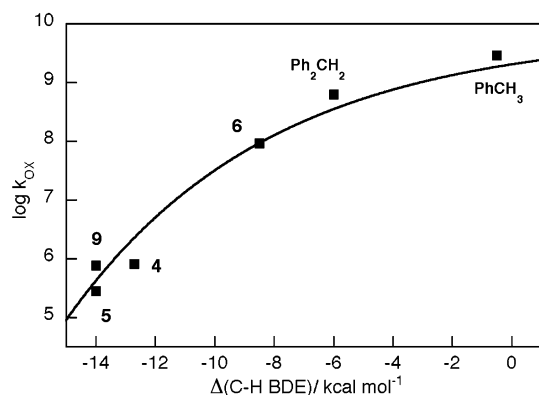
The five-member ring moiety of all the structures in this paper leads to an enhancement of the hydrocarbon reactivity toward alkoxy radicals by approximately a factor of 6, as judged from the comparison of values for **1** and **6** with those for diphenylmethane (see Tables 1 and 2). Further stabilization by additional phenyl groups only led to an enhancement of about a factor of 2, as based on the comparisons of **5** with **4** and of **9** with **6**. Interestingly, steric effects (compare **6** and **8**) are comparable with those for reaction of radicals with oxygen (see Table 3).

It is well-known that several heteroatom-centered radicals do not react with oxygen. Examples of this situation are alkoxy, phenoxy, and hydrazyl radicals.

(20) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992–4996.

(21) Chateaufneuf, J.; Luszyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629–1632.

(22) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983–4992.



**FIGURE 6.** Plot of the logarithm of the rate constants for the reaction of various radicals with oxygen against the difference between the CH bond strength in toluene and in the substrate. Numbering according to Chart 1.

In extreme cases where other parameters come into play (e.g., steric hindrance and resonance stabilization) the radicals are sufficiently stable to be isolated, and in cases such as hindered nitroxides, galvinoxyl and diphenylpicryl hydrazyl (DPPH) are commercially available.

The reaction of benzyl radicals with oxygen ( $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) is irreversible at room temperature;<sup>23</sup> only the cases involving high-resonance delocalization, such as triphenylmethyl radical, lead to reversible reaction with oxygen.<sup>8</sup> For the triphenylmethyl radical steric effects force all rings into a propeller-like conformation, where the rings are not in the preferred orientation for maximum electron delocalization. Thus, the oxygenation rate with benzylic radicals can reflect aspects related to the spin density at the benzylic position, the radical stabilization through spin delocalization, stereoelectronic effects, and steric effects in the reaction with oxygen.

The C–H bond dissociation energy (BDE) is a good measure of the stabilization energy of benzyl radicals: it is clear that a stronger bond generates a less stable radical. In this way, the relationship between  $k_{\text{OX}}$  and the corresponding bond dissociation energies can give us information about the importance of the stereoelectronic effects. Thus, the logarithm of  $k_{\text{OX}}$  was plotted against C–H BDE relative to toluene previously reported by Bordwell et al. (Figure 6).<sup>24–26</sup>

Radicals generated from diphenylmethane, fluorene, 3-phenylindene, 1,3-diphenylindene, and phenylfluorene showed a good correlation with  $\log k_{\text{OX}}$ , thus, no other factors appear relevant in determining the reactivity with oxygen than the stability of these radicals. In the case of the benzyl radical the value of  $k_{\text{OX}}$  approaches the diffusion limit. Interestingly the reactivity of the radical from **4** is very modest; here spin delocalization into the  $\pi$  system must be responsible for the low reactivity with oxygen.

(23) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

(24) An error of  $\pm 3$  kcal/mol has been associated with the C–H BDE measurements. The BDE for 1,3-diphenylindene was assumed to be equal to the C–H BDE in 9-phenylfluorene.

(25) Bordwell, F. G.; Harrelson, J. A.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105.

(26) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1992**, *114*, 10173–10176.

Finally, the rate constants for the trapping of the stabilized carbon-centered radicals derived from Ciba Irganox HP-136, 9-carbomethoxyfluorene, **5**, **8**, and **9** with the persistent nitroxide TEMPO were at least three hundred times slower than those for benzyl radicals. It is clear that in the case of radical **8**, where no reaction was observed, the lack of reactivity must be due to steric hindrance; in contrast, reactions with oxygen and with *tert*-butoxyl were slowed, but still observable. Resonance stabilization for **5** and **9** radicals appears to be the most important factor responsible for the highly reduced reactivities toward TEMPO and oxygen.

### Experimental Section

**Reagents.** TEMPO, indane, indene, fluorene, and 9-phenylfluorene were commercially available. Ciba Irganox HP-136 was a gift from CIBA Specialty Chemicals. Di- $\alpha$ -cumyl hypoxynitrite,<sup>16</sup> 1-phenylindane,<sup>27</sup> 3-phenyl-1-indene,<sup>28</sup> 1,3-diphenylindene,<sup>29</sup> 9-chlorofluorene,<sup>30</sup> and 9-*tert*-butylfluorene<sup>31</sup> were prepared by literature methods.

**Laser Flash Photolysis.** The radicals were generated from the corresponding compounds by laser excitation of di-*tert*-

butyl peroxide in benzene, using the 355-nm pulses from a Continuum Nd:YAG Surelite. Excitation at 266 nm from a Continuum Nd:YAG Surelite laser (fourth harmonic, <10 ns, 20 mJ/pulse) was used for direct photolysis of haloalkane **7**. Transient signals were captured with a digital oscilloscope that was interfaced to a computer, which also controlled the experiment. The system was operated with software written in the LabVIEW 5.1 environment from National Instruments. All experiments were carried out with use of static cells constructed from 7 × 7 mm Suprasil quartz tubing. Samples were purged with a slow stream of either nitrogen or oxygen, as required.

**Acknowledgment.** J.C.S. thanks the Natural Sciences and Engineering Research Council of Canada and Imperial Oil Canada for generous support. E.F.S. thanks the Spanish Ministry of Education for a grant.

JO0266660

---

(28) Halterman, R. L.; Zhu, C. *Tetrahedron Lett.* **1999**, *40*, 7445–7448.

(29) Casuscelli, F.; Chiacchio, U.; Liguori, A.; Romeo, G.; Sindona, G.; Uccella, N. *Tetrahedron* **1993**, *49*, 5147–5152.

(30) Hurd, C. D.; Mold, J. D. *J. Org. Chem.* **1948**, *13*, 339–346.

(31) Streitwieser, A. J.; Chang, C. J.; Reuben, D. M. E. *J. Am. Chem. Soc.* **1972**, *94*, 5730–5734.

---

(27) Valyocsik, E. W.; Sigal, P. *J. Org. Chem.* **1971**, *36*, 66–72.