vation in different solvents[29] and has been recommended for use in nonaqueous solvents.[30] For a particular series of experiments the standard $E_{1/2}$ value for this couple could vary by as much as 20 mV. The value needed to correct to 0.875 V was applied in these experiments when appropriate. The potentials were generally reproducible to ±10 mV, ≥5 mV for consecutive scans, and 20 mV for different investigators. The uncertainty in using the X-Y recorder has been estimated to be 5–10 mV.[31]

When oxidation potentials of neutral compounds were recorded, it was often necessary to polish the electrode between each scan to obtain consistent E_{ox} values. This was not a problem in working with anionic species.

Acknowledgment. This research was supported by the National Science Foundation. A generous gift of dimethyl sulfoxide was provided by the Chemical Division of Crown Zellerbach, Camus, WA. We express our appreciation to Professor V. D. Parker for providing us with the results of a kinetic isotope study for the reaction of **1** with pyridine.

Registry No. **1**, 42523-30-8; **2**, 51548-21-1; **7**, 7235-14-5; **8** (G = H), 34985-70-1; **8** (G = 2-Br), 113533-34-9; **8** (G = 4-aza), 113548-07-5; **8** (G = 3-Me), 113533-35-0; **8** (G = 2-Me), 113533-36-1; **8** (G = 3-MeO), 113533-37-2; **8** (G = 2-PhS), 113533-38-3; **8** (G = 3,6-(MeO)$_2$), 113566-63-5; **8** (G = 2-MeO), 101631-12-3; **8** (G = 2,7-(PhS)$_2$), 113533-39-4; **8** (G = 2-Me$_2$N), 113533-40-7; **8** (G = 2,3,6,7-(MeO)$_4$), 65989-21-1; TTF, 31366-25-3; FlH$_2$, 86-73-7; FlH$^-$, 12257-35-1; 2-Br-FlH$_2$, 1133-80-8; 2-Br-FlH$^-$, 85535-20-2; 4-aza-FlH$_2$, 244-99-5; 4-aza-FlH$^-$, 100858-92-2; 3-Me-FlH$_2$, 2523-39-9; 3-Me-FlH, 100858-85-3; 2-Me-FlH$_2$, 1430-97-3; 2-Me-FlH$^-$, 100858-86-4; 3-MeO-FlH$^-$, 100858-84-2; 2-PhS-FlH$_2$, 59014-81-2; 2-PhS-FlH$^-$, 113533-29-2; 3,6-(MeO)$_2$-FlH$_2$, 96617-41-3; 3,6-(MeO)$_2$-FlH$^-$, 113533-30-5; 2-MeO-FlH$_2$, 2523-46-8; 2-MeO-FlH$^-$, 100858-88-6; 2,7-(PhS)$_2$-FlH$_2$, 59014-86-7; 2,7-(PhS)$_2$-FlH$^-$, 113533-31-6; 2,7-(OMe)$_2$-FlH$^-$, 100858-87-5; 2,3,6,7-(MeO)$_4$-FlH$_2$, 51487-65-1; 2,3,6,7-(MeO)$_4$-FlH$^-$, 113533-32-7; 2-Me$_2$N-FlH$_2$, 13261-62-6; 2-Me$_2$N-FlH$^-$, 113533-33-8; 9-Ph-FlH, 789-24-2; 9-Ph-Fl$^-$, 31468-22-1; 9-Ph-Fl$^{\bullet+}$, 113566-64-6; 9-(*p*-MeC$_6$H$_4$)-FlH, 18153-43-0; 9-(*p*-MeC$_6$H$_4$)-Fl$^-$, 42730-14-3; 9-(*p*-MeC$_6$H$_4$)-Fl$^{\bullet+}$, 113533-46-3; 9-(*m*-ClC$_6$H$_4$)-FlH, 32377-11-0; 9-(*m*-ClC$_6$H$_4$)-Fl$^-$, 73872-45-4; 9-(*m*-ClC$_6$H$_4$)-Fl$^{\bullet+}$, 113533-47-4; 9-MeS-FlH, 18153-40-7; 9-MeS-Fl$^-$, 85535-28-0; 9-MeS-Fl$^{\bullet+}$, 113533-48-5; 2,7-(MeO)$_2$-9-Ph-FlH, 113533-41-8; 2,7-(MeO)$_2$-9-Ph-Fl$^-$, 113533-44-1; 2,7-(MeO)$_2$-9-Ph-Fl$^{\bullet+}$, 113533-50-9; 3,6-(MeO)$_2$-9-MeS-FlH, 113533-28-1; 3,6-(MeO)$_2$-9-MeS-Fl$^-$, 113533-45-2; 3,6-(MeO)$_2$-9-MeS-Fl$^{\bullet-}$, 113533-51-0; 1,2-benzo-FlH$_2$, 238-84-6; 1,2-benzo-FlH$^-$, 113533-42-9; 1,2-benzo-Fl$^{\bullet+}$, 113566-65-7; 2,3-benzo-FlH$_2$, 243-17-4; 2,3-benzo-FlH$^-$, 113533-43-0; 2,3-benzo-Fl$^{\bullet+}$, 113566-66-8; pyridine, 110-86-1; deuterium, 7782-39-0; 3,6-dimethoxyfluorenone, 13235-07-9; 2,3,6,7-tetramethoxyfluorenone, 58532-06-2; mesitylmagnesium bromide, 2633-66-1; 9-mesityl-9-hydroxyfluorene, 113533-27-0; fluoradene, 205-94-7; fluoradene anion, 70606-47-2; fluoradene radical cation, 113533-49-6.

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[29] Koepp, H.-M.; Wendt, H.; Strelow, H. *Z. Electrochem.* **1960**, *64*, 483–491. Schneider, H.; Strelow, H. *J. Electroanal. Chem.* **1966**, *12*, 530–534.

[30] Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527–1532.

[31] Baiser, M. M.; Lund, H. *Organic Electrochemistry*, 2nd ed.; Marcel Dekker: New York, 1983; Chapter 3, p 81.

Acidities of Radical Cations Derived from Cyclopentadienes and 3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes

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Abstract: Radical cation acidities of nine cyclopentadienes and six 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes have been estimated with the equation $\mathrm{p}K_{\mathrm{HA}^{\bullet+}} = \mathrm{p}K_{\mathrm{HA}} + [E_{ox}(\mathrm{A}^-) - E_{ox}(\mathrm{HA})]23.06/1.37$. Introduction of Ph substituents into the 2- and 5-positions of cyclopentadiene (CpH$_2$) caused the acidity of its radical cation ($\mathrm{p}K_{\mathrm{HA}^{\bullet+}}$) to decrease from −17 to −8. This decrease is the net result of stabilization (by delocalization) of the positive charge and odd electron in the radical cation (acid weakening) and stabilization of its conjugate base, the radical (acid strengthening). The other effects of structural changes on radical cation acidities observed can be rationalized in a similar manner. Most notable are the 11 and 8.5 $\mathrm{p}K_{\mathrm{HA}^{\bullet+}}$ unit decreases in the acidities observed for the radical cations derived from 1,2,3,4,5-pentamethyl- and 1,2,3,4,5-pentaphenylcyclopentadienes, respectively, relative to CpH$_2^{\bullet+}$. An open-chain analogue of Ph$_5$CpH, 1,1,3,5,5-pentaphenyl-1,4-pentadiene, is 10.9 p*K* units less acidic because of lesser carbanion stabilization, but its radical cation is 11.5 p*K* units more acidic because of lesser cation stabilization. A 13 p*K* unit acid-weakening effect of the 4-Me$_2$N group in 4-Me$_2$NC$_6$H$_4$CH(CH=CPh$_2$)$_2^{\bullet+}$ is associated with loss of an electron from the lone pair on nitrogen in 4-Me$_2$NC$_6$H$_4$CH(CH=CPh)$_2$, whereas the parent radical cation, C$_6$H$_5$CH(CH=CPh$_2$)$_2^{\bullet+}$, is formed by loss of an electron from an alkene π bond in C$_6$H$_5$CH(CH=CPh$_2$)$_2$. A plot of $E_{ox}(\mathrm{A}^-)$ vs $\mathrm{p}K_{\mathrm{HA}}$ was found to be linear with a slope near unity for 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes. Homolytic bond dissociation energies for the acidic C–H bonds in these 15 hydrocarbons are estimated from the $\mathrm{p}K_{\mathrm{HA}}$ and $E_{ox}(\mathrm{A}^-)$ data. Several striking examples of substituents having opposite effects on homolytic and heterolytic BDEs were observed.

The method developed recently to estimate acidities for the radical cations derived from phenothiazines and fluorenes[1] has now been extended to cyclopentadiene, pentamethylcyclopentadiene, cyclopentadienes bearing two, four, or five phenyl rings, and several 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes.

Results

Cyclopentadienes. The oxidation potentials of several cyclopentadienide anions, $E_{ox}(\mathrm{A}^-)$, the acidities of their conjugate acids, $\mathrm{p}K_{\mathrm{HA}}$, and the oxidation potentials of these acids, $E_{ox}(\mathrm{HA})$, are summarized in Table I.

The $\mathrm{p}K_{\mathrm{HA}^{\bullet+}}$ values in Table I were calculated from eq 1 by using the data in Me$_2$SO whenever possible. It was necessary to use MeCN as the solvent to measure $E_{ox}(\mathrm{HA})$ for cyclopentadiene

$$\mathrm{p}K_{\mathrm{HA}^{\bullet+}} = \mathrm{p}K_{\mathrm{HA}} + [E_{ox}(\mathrm{A}^-) - E_{ox}(\mathrm{HA})]23.06/1.37 \qquad (1)$$

(CpH$_2$) because it oxidizes near the potential for the Me$_2$SO solvent. This increases the uncertainty of the $\mathrm{p}K_{\mathrm{HA}^{\bullet+}}$ for CpH$_2^{\bullet+}$ somewhat, since E_p values in MeCN for $E_{ox}(\mathrm{HA})$ are 70–90 mV more positive for 2,5-diphenylcyclopentadiene and its derivatives in MeCN than in Me$_2$SO (Table I), and this may be true for cyclopentadiene itself. CV measurements with CpH$_2$ required

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[1] (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473–2474. (b) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* preceding paper in this issue.

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Table I. Acidity and Oxidation Potential Values for Cyclopentadienes at 25 °C

		$E_{ox}(HA)^b$		$E_{ox}(A^-)^b$		
cyclopentadiene	$pK_{HA}{}^a$	MeCN	Me_2SO	MeCN	Me_2SO	$pK_{HA}{}^{\bullet + d}$
cyclopentadiene	18.0	2.23		0.096	0.153	-17^e
		(0.10)		(0.055)	(0.045)	
2,5-Ph_2	14.3	1.51	1.42	0.075	0.112	−8
		(0.06)	(0.07)	(0.05)	(0.045)	
2-(4-MeOPh)-5-Ph	15.2	1.31	1.24	0.004	0.022	−5
		(0.07)	(0.07)	(0.055)	(0.045)	
2-(4-MePh)-5-Ph	14.8	1.42	1.34	0.042	0.066	−7
		(0.06)	(0.08)	(0.055)	(0.045)	
2-(3-MeOPh)-5-Ph	14.1		1.41		0.120	−8
			(0.075)		(0.04)	
2-(4-ClPh)-5-Ph	13.5		1.43		0.165	−8
			(0.075)		(0.04)	
2,3,4,5-Ph_4	13.2	1.54	1.55	0.202	0.232	−9
		(0.10)	(0.07)	(0.055)	(0.04)	
1,2,3,4,5-Ph_5	12.5	1.68	1.58	0.314^c	0.333^c	−8.5
		(0.09)	(0.07)	(0.075)	(0.055)	
1,2,3,4,5-Me_5	26.1	1.43	1.42		−0.504	−6.5
		(0.065)	(0.08)		(0.04)	

[a] Measured in Me_2SO against one or two standard acids or indicators. [b] Irreversible oxidation potentials measured vs a Ag/AgI electrode with a ferrocene–ferrocenium standard under conditions previously described.[1] Wave widths ($E_p - E_{p/2}$) are given in parentheses. [c] Reversible peak reported as an E_p value. [d] Calculated from data in Me_2SO by using eq 1. [e] Calculated by using $E_{ox}(HA)$ data in MeCN; if $E_{ox}(HA)$ is 90 mV more negative in Me_2SO, as is true for 2,5-Ph_2-CpH_2, $pK_{HA^{\bullet +}} = -15.5$.

careful polishing of the electrode after each scan because of electrode fouling. The substituted cyclopentadienes caused less trouble in this regard. Cyclopentadienide ions did not cause electrode fouling and gave narrower CV waves ($E_p - E_{p/2} = 45$ mV in Me_2SO, 55 mV in MeCN). The E_p values were usually 20–40 mV more negative in MeCN than in Me_2SO, but for the neutral acids, when a shift occurred, it was usually larger and in the reverse direction (Table I).

The $E_{ox}(A^-)$ value we observed for the CpH^- ion in Me_2SO (no significant ion pairing to the K^+ counterion) is about 160 mV *more positive* (when corrected for the difference in reference electrodes) than is the $E_{ox}(A^-)$ value reported for the corresponding lithium salt in THF containing 17% HMPA at −62 °C (−0.37 V vs SCE).[2,3] (A value of −0.43 V vs SCE in 90:10 THF/HMPA at −30 °C was also reported.[2] The 60 mV positive shift at higher HMPA concentration reported suggests that the HMPA may be causing a shift in wave position as well as causing dissociation of the Li^+CpH^- ion pair.) Despite the difference in $E_{ox}(A^-)$ values in Me_2SO and THF/HMPA solvents, the $E_{ox}(A^-)$ values for CpH^- relative to Ph_3C^- agree to within 20 mV, as will be brought out later. This indicates that measurements in THF/HMPA are for the free anions rather than ion pairs. The $E_{ox}(A^-)$ value of −0.49 V vs SCE reported for $Li^+Me_5Cp^-$ in THF/HMPA[4] is not in relative agreement with that of Me_5Cp^- ion in Me_2SO, however. The $\Delta E_{ox}(A^-)$ in Me_2SO is 0.657 V (Table I), whereas that in THF/HMPA is only 0.12 V. It would appear that in the latter instance the Li^+ counterion may be strongly influencing the potential.

3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes. The acidity and oxidation potential data for these compounds and their conjugate bases are presented in Table II. The equilibration of these hydrocarbons with their indicator anions was very slow, presumably because of the appreciable solvent and molecular reorganization required to form these severely crowded anions. The cyclic voltammograms for the anion oxidations were reversible, a property that may be associated with steric hindrance to dimerization in the severely crowded radicals being formed. The wave widths were near 60 mV in both Me_2SO and MeCN, but the potentials were about 75 mV more positive in MeCN. This is opposite to the shifts observed for cyclopentadienes. The high $E_{ox}(HA)$ values for most of the hydrocarbons made it necessary to make the CV measurements in MeCN rather than in Me_2SO.

Table II. Acidity and Oxidation Potential Values for 3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes, $G\text{-}C_6H_4CH(CH{=}CPh_2)_2$ in Me_2SO at 25 °C

			$E_{ox}(A^-)^e$		
G	$pK_{HA}{}^a$	$E_{ox}(HA)^c$	MeCN	Me_2SO	$pK_{HA^{\bullet +}}{}^g$
H	23.4	2.15	−0.362	−0.434	−20
		(0.060)	(0.060)	(0.060)	
4-NMe_2	25.5^b	1.39^d		−0.56	−7
		(0.055)		(0.070)	
4-Me	23.9	2.03	−0.388	−0.465	−18
		(0.050)	(0.060)	(0.055)	
4-F	23.3	2.16	−0.350	−0.413	−20
		(0.045)	(0.065)	(0.055)	
3,4-Cl_2	21.4	2.23	−0.244	−0.320	−21.5
		(0.065)	(0.060)	(0.060)	
3-NO_2	21.2^b	2.28	−0.226	-0.301^f	−22
		(0.090)	(0.065)	(0.060)	

[a] The equilibrations of these hydrocarbons with indicator anions were unusual in that they required minutes or even hours rather than seconds. [b] Calculated from a four-point Hammett plot, $\rho = 2.5$. [c] Irreversible potentials measured in MeCN under the conditions reported in ref 1. [d] Reversible. [e] Reversible potentials reported as E_p values. [f] Partially reversible. [g] Calculated from the equation $pK_{HA^{\bullet +}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23/1.37$. These values have not been corrected for a possible positive shift in $E_{ox}(HA)$ values caused by a shift from Me_2SO to MeCN solvent nor for the positive shift in $E_{ox}(A^-)$ values, relative to $E_{ox}(HA)$ values, resulting from their reversibility.

The errors in pK_{HA} measurements are usually about ±0.1 pK_a unit, and the reproducibility in making $E_{ox}(A^-)$ and $E_{ox}(HA)$ CV measurements is usually about 10 mV for a single investigator (20 mV for separate investigators). The irreversibility of the $E_{ox}(A^-)$ and $E_{ox}(HA)$ waves causes cathodic shifts of about 50 mV, which tend to cancel. When these sources of error are considered, together with the uncertainty introduced by differences in CV wave shapes and the use of different solvents for $E_{ox}(HA)$ and $E_{ox}(A^-)$ measurements, we conclude that the $pK_{HA^{\bullet +}}$ values calculated in Table I are accurate to about ±2 units.[5]

Discussion

Substituent Effects on Acidities of Cyclopentadiene. Cyclopentadiene has a pK_a of 18.0 in Me_2SO.[6] This is an absolute value in the sense that it is based on Me_2SO as a standard state.

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(2) Juan, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748.

(3) $E_{Ag/AgI} = E_{SCE} + 0.365$.

(4) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470–1472.

(5) Cheng, J.-P. Ph.D. Dissertation, Northwestern University, June, 1987.

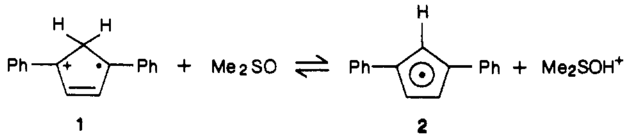
(6) (a) Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632–635. (b) Bordwell, F. G.; Drucker, G. E.; Andersen, N. H.; Denniston, A. D. *J. Am. Chem. Soc.* **1986**, *108*, 7310–7313.

A pK_a of 16 has been reported in H_2O[7] and an ion pair pK_a of 16.2 (15.3 when anchored on the Me_2SO scale[6b]) in cyclohexylamine (CHA).[7] A pK_a of 22–23, relative to that of Ph_3CH in CHA, has been calculated from difference in homolytic bond dissociation energies (BDEs) and oxidation potentials of the anions, $E_{ox}(A^-)$, in THF/HMPA.[2] This method can be used to calculate the pK_a of CpH_2 in Me_2SO from the difference in $E_{ox}(A^-)$ values in Me_2SO for Ph_3C^-, −0.611 V,[5] and CpH^-, 0.153 V (Table I), together with the difference in BDEs for Ph_3CH and CpH_2. The $\Delta E_{ox}(A^-)$ value in Me_2SO is −0.764 V (vs Ag/AgI), which is in good agreement with the $\Delta E_{ox}(A^-)$ value of −0.785 V in THF/HMPA (vs SCE electrode).[2] Recently, we have estimated the BDE of Ph_3CH to be about 81 kcal/mol in Me_2SO,[8] rather than 75 kcal/mol, the value used in the earlier calculation.[2] Since the gas-phase (and solution-phase[8]) BDE of CpH_2 is also about 81,[9] the ΔpK_a between Ph_3CH and CpH_2 can be equated with $\Delta E_{ox}(A^-)$, which is 17.6 kcal/mol or 12.8 pK_a units. The calculated pK_a for CpH_2 in Me_2SO is then 30.6 − 12.8 = 17.7. (Other calculated pK_as based on the Ph_3CH BDE of 75[2] must also be lowered by about 4 units.)

Examination of Table I shows that the presence of Ph groups at the 2- and 5-positions of CpH_2 increases the acidity by 3.7 pK_a units. The presence of a 3-MeO or 4-Cl group in one of the rings causes a small additional acidity increase, and a 4-MeO or 4-Me group has the opposite effect, as expected. Introduction of two or three additional Ph groups causes only 1.1 and 1.8 pK units additional increase because severe crowding prevents effective overlap of the Ph groups with the planar cyclopentadienide ring.

The presence of five Me groups in the cyclopentadienyl ring causes a decrease in acidity of 8.1 pK units.[10] (A 7.3-unit decrease has also been observed for 1,2,3,4,5,6,7-heptamethylindene, relative to indene.[10]) This acid-weakening effect is believed to be caused by methyl hyperconjugative stabilization in the undissociated acid coupled with steric inhibition of solvation in the anion. It leads to significant increases in the electron-donor strength of the Me_5Cp ligand vs the CpH ligand in metal complexes.[4,10]

Radical Cation Acidities of Cyclopentadienes. Application of eq 1 to cyclopentadiene reveals that the corresponding radical cation has a high acidity, comparable to that of fluorene radical cation, $pK_{HA^{\bullet+}} = -17$ (Table I). We have seen in the preceding paper that introduction of 2- and 7-MeO substituents into the fluorene radical cation delocalizes the positive charge and odd electron, causing a sharp increase in $pH_{HA^{\bullet+}}$, from −17 to −6.[1b] The 2- and 5-Ph groups in 2,5-diphenylcyclopentadiene cause a similar effect for the same reason (Table I, eq 2).



1 2

(2)

The two Ph groups cause a negative shift in $E_{ox}(HA)$ in MeCN of 720 mV, equivalent to 16.6 kcal/mol, relative to that of CpH_2 itself (Table I). This could result in a 12 $pK_{HA^{\bullet+}}$ unit decrease in acidity, but it is offset to some degree by the radical-stabilizing effects of the Ph groups in **2**, which are acid strengthening. The size of this effect is determined by changes in pK_{HA} and $E_{ox}(A^-)$ in eq 1, which, when combined provide an estimate of radical stabilization by the ΔAOP method (eq 3).[11] The ΔAOP method

$$\Delta AOP = 1.37\Delta pK_{HA} + 23.06\Delta E_{ox}(A^-) \quad (3)$$

assumes that the change in basicity of the anion (ΔpK_{HA}) caused by introduction of two Ph groups will cause an equivalent change (in kilocalories per mole) in its oxidation potential, $\Delta E_{ox}(A^-)$, in the absence of radical-stabilizing effects. (This assumption is based on the observation of examples of linear plots of $E_{ox}(A^-)$ vs pK_a for (1) 2- and 2,7-substituted fluorenide ions,[11] (2) 10-substituted 9-methylanthracenide ions,[5] and (3) 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienide ions (Figure 1). In each instance the remote substituents cause little or no stabilization of the radical.) For the change from CpH_2 to 2,5-$(Ph)_2$-CpH_2, ΔAOP = −5.07 + 0.94 = −4.1 kcal/mol, which indicates a radical-stabilizing effect of about 4 kcal/mol. This should produce an acid-strengthening effect of about 3 $pK_{HA^{\bullet+}}$ units, which when combined with the 16.6 kcal/mol (12 $pK_{HA^{\bullet+}}$ unit) acid-weakening effect leads to a net 9 $pK_{HA^{\bullet+}}$ unit decrease in acidity observed (Table I).

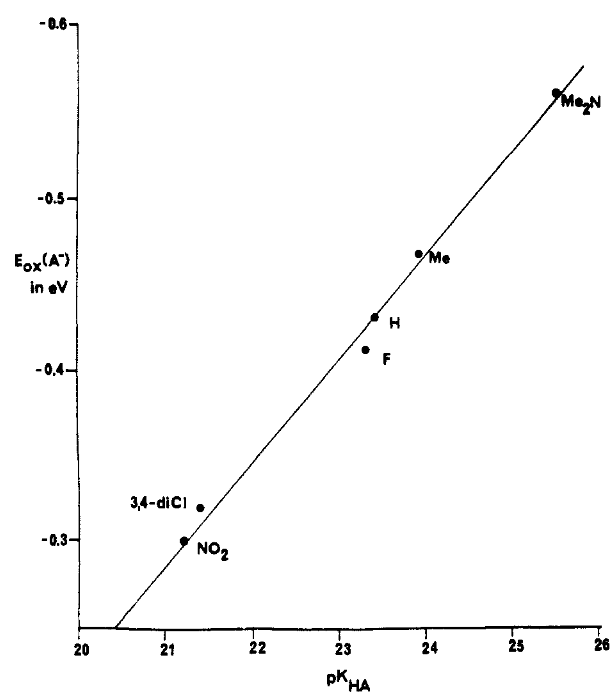


Figure 1. Least-squares plot of the oxidation potentials of 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienide ions vs the equilibrium acidities of their conjugate acids, both measured in Me_2SO solution at 25 °C (data from Table II).

What effect will a change from Me_2SO to MeCN have on these pK_{HA} and $pK_{HA^{\bullet+}}$ values? Relative acidities within a family are generally independent of solvent, so we would expect little difference in ΔpK_{HA} (or $\Delta pK_{HA^{\bullet+}}$) values between CpH_2 and 2,5-$(Ph)_2$-CpH_2. On the other hand, if the effect on a given acid, such as radical cation **1**, is to be evaluated, the changes in solvation of **1**, **2**, and the proton must all be considered. The solvent switch should have little effect on **2**, a small effect on the stability of **1**, and about a 5.5 kcal/mol decrease in the solvation of the proton.[12]

The introduction of either a MeO or Me group into the 4-position of one of the Ph groups in 2,5-diphenylcyclopentadiene causes a small decrease in the acidity of the radical cation (Table I). These groups cause negative shifts in $E_{ox}(HA)$ of 180 and 80 mV, respectively, which lead to decreases in radical cation acidities of 3 and 1.3 pK units, respectively. The offsetting radical-stabilizing effects of 4-MeO and 4-Me, calculated by the ΔAOP method, are 0.85 and 0.4 kcal/mol, respectively. (These small radical-stabilizing effects are comparable to those observed for the remote (para) effects of these groups observed for fluorenes.[11]) The effects of 3-MeO or 4-Cl substituents in stabilizing either radical cations or radicals appear to be negligible, which is in agreement with the observations in fluorenes and arylacetonitriles.[11]

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[7] Streitwieser, A., Jr.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188–2190. This paper also contains a good discussion of earlier estimates of the pK_a of cyclopentadiene.

[8] Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.

[9] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

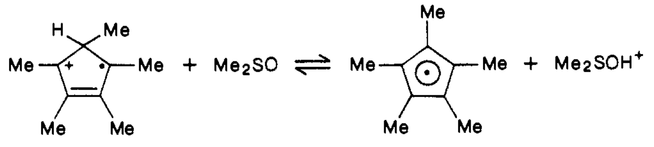
[10] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6188–6189.

[11] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

[12] Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1972**, *76*, 2024–2034. Some organic cations are stabilized by a switch from Me_2SO to MeCN (e.g., Et_4N^+ and Bu_4N^+), but others are destabilized (e.g., Ph_4As^+, Cs^+).

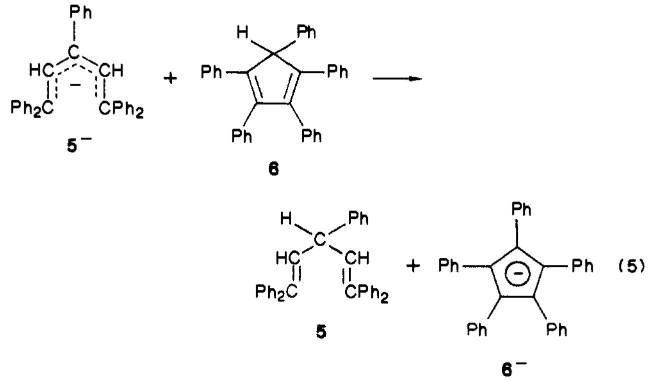
The introduction of additional Ph substituents into 2,5-diphenylcyclopentadiene, as in 2,3,4,5-tetraphenyl- or 1,2,3,4,5-pentaphenylcyclopentadiene, causes a slight increase in the acidities of the corresponding radical cations (Table I). Steric hindrance in these molecules causes twisting of the Ph groups so that but little additional stabilization is provided to the radical cation, radical, or carbanion, as is brought out by the pK_{HA} and electrochemical data in Table I. Oxidation of the 1,2,3,4,5-pentaphenyl carbanion either with chemical oxidants or by electrochemical means gives a persistent purple radical. Examination of scalar molecular models reveals that large steric effects are also present in the 1,2,3,4-tetraphenylcyclopentadienyl ion and radical species, but there is no evidence to indicate that the radical species is persistent. This illustrates once again the importance of steric effects in causing radicals to be persistent.[13]

The stabilizing effects of the four methyl groups in the Me_5-$CpH^{\bullet+}$ radical cation **3** (eq 3) amount to 18.4 kcal/mol, as judged by the 800 mV negative shift of E_{ox}(HA) of Me_5-CpH relative to that of cyclopentadiene CpH_2. This could cause a 13.5 p$K_{HA^{\bullet+}}$ unit decrease in acidity, but this is offset by a 4 kcal/mol stabilization of radical **4** (eq 3), attributable to the fifth methyl group. (The Me group in 9-MeFl$^{\bullet}$ is estimated to cause a 4.5 kcal/mol stabilizing effect.[11]) The combination of these acid-weakening and acid-strengthening effects gives rise to a net 10.5 unit decrease in p$K_{HA^{\bullet+}}$ (eq 4), estimated by eq 1 (Table I).



(4)

3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes. Examination of Table II shows that 1,1,3,5,5-pentaphenyl-1,4-pentadiene (**5**), an open-chain analogue of 1,2,3,4,5-pentaphenylcyclopentadiene (**6**) is 10.9 pK units less acidic. This 15 kcal/mol difference (eq 5) corresponds roughly to the resonance energy of the cyclopentadiene ring.[6a]



(5)

$\Delta G° \simeq -15$ kcal/mol

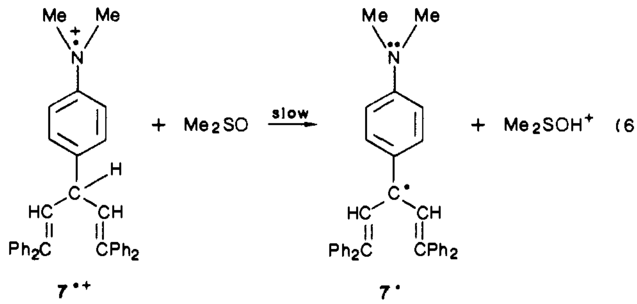
Steric effects cause the Ph groups in both the carbanions **5**$^-$ and **6**$^-$ to be twisted, which prevents effective delocalization of the negative charge into the Ph rings. The absence of delocalization to the 3-aryl group in anion **5**$^-$ is evident from the small Hammett ρ calculated from the pK_a data (2.5) relative to ρ's in Me_2SO for acidities of other benzylic systems, such as $ArCH_2Ph$ or $ArCH_2CN$ ($\rho \simeq$ 5–6). The absence of effective overlap in corresponding radical **5**$^{\bullet}$ is made evident by a ΔAOP value of zero calculated for the 4-Me_2N group from the $E_{ox}(A^-)$ and pK_{HA} values for the 4-$Me_2NC_6H_4C^-(CH{=}CPh_2)_2$ anion, relative to that of the parent. (A ΔAOP of the order of 4 kcal/mol would have been expected for a planar radical by analogy with that observed for the 4-Me_2N group in the $ArCH_2CN$ system.[11]) The reversibility of the $E_{ox}(A^-)$ CV measurements for the 3-$ArC^-(CH{=}CPh_2)_2$ carbanions (Table II) suggests that the radicals formed have an unusually long lifetime in solution, which is consistent with steric inhibition of dimerization.

Table III. Bond Dissociation Energies (BDEs) in Me_2SO for Cyclopentadienes and 3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes G-$C_6H_4CH(CH{=}CPh_2)_2$

cyclopentadiene	BDE[a]	G in G-C_6H_4CH-$(CH{=}CPh_2)_2$	BDE[b]
cyclopentadiene	81.2	H	75.0
2,5-Ph_2	75.15	4-NMe_2	75.0
2-(4-MeOPh)-5-Ph	74.3	4-Me	75.0
2-(4-MePh)-5-Ph	74.8	4-F	75.4
2-(3-MeOPh)-5-Ph	75.1	3,4-Cl_2	74.9
2,3,4,5-Ph_4	76.8	3-NO_2	75.1
1,2,3,4,5-Ph_5	77.8[b]		
1,2,3,4,5-Me_5	77.1		

[a] Calculated from eq 6. [b] Not corrected for reversibility.[15]

The 0.57 V (13.1 kcal/mol) more positive E_{ox}(HA) value for **5** than **6** is associated with the much more localized positive charge and odd electron in radical cation **5**$^{\bullet+}$ than in **6**$^{\bullet+}$. This, in turn, leads to the 11.5 pK unit greater acidity of **5**$^{\bullet+}$ than **6**$^{\bullet+}$. Introduction of 4-Me, 4-F, 3,4-$(Cl)_2$, or 3-NO_2 substituents into the 3-Ph ring of **5**$^{\bullet+}$ has relatively little effect on the acidity of radical cation of **5**$^{\bullet+}$. This is not surprising, since substituents in the 3-Ph ring cannot interact directly with the positive charge in the radical cation. The 13 pK unit decrease of the acidity of the radical cation when a 4-Me_2N group is introduced indicates powerful stabilization of the radical cation by Me_2N. It seems likely that in this instance the oxidation involves loss of an electron from the lone pair on nitrogen, giving radical cation **7**$^{\bullet+}$, rather than loss of an electron from one of the π bonds in the diene system, as is the case for the formation of **5**$^{\bullet+}$ and its other derivatives. For 4-$Me_2NC_6H_4CH(CH{=}CPh_2)_2$ both E_{ox}(HA) and $E_{ox}(A^-)$ were reversible. Both the radical cation **7**$^{\bullet+}$ and the radical **7**$^{\bullet}$ are apparently slow to dimerize, and deprotonation of **7**$^{\bullet+}$ by the Me_2SO (eq 6) also must occur slowly. The E_{ox}(HA) value for 4-$Me_2NC_6H_4CH(CH{=}CPh_2)_2$, when compared with that of the unsubstituted parent, reveals a 17 kcal/mol stabilization of radical cation **7**$^{\bullet+}$, which leads to a 13 pK unit decrease in acidity.



(6)

The importance of steric effects, rather than stabilization by delocalization, in making radical **7**$^{\bullet}$ persistent is brought out by the failure of delocalization to occur into the 4-$Me_2NC_6H_4$ moiety to an extent sufficient to allow stabilization by the Me_2N group, giving rise to ΔAOP = 0.

Correlation of $E_{ox}(A^-)$ and pK_{HA} Values. A plot of $E_{ox}(A^-)$ for 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes vs the acidities of their conjugate acids is linear (Figure 1). The slope of the plot is near unity when both axes are in kilocalories per mole. this means that the substituents are exerting neither a radical stabilizing nor radical destabilizing effect on the oxidation of the anion on the electrode and that changes in the oxidation potentials can be correlated directly by changes in basicity; i.e., for every 1 kcal/mol increase in basicity there is a corresponding 1 kcal/mol increase (negative shift) in the oxidation potential. Closely similar correlations have been found in two other instances, 2-substituted fluorenide ions[11] and 10-substituted 9-methylanthranide ions.[5] The existence of these direct $E_{ox}(A^-)$ vs pK_{HA} correlations in three instances indicates that such direct relationships are general in hydrocarbon families where steric effects are constant and radical-stabilizing effects are small.

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[13] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *8*, 13–18.

Table IV. Properties of 3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes $G\text{-}C_6H_4CH(CH{=}CPh_2)_2$

G	mp, °C	NMR ($CDCl_3$), δ			
4-Me	164–165	2.3 (3 H, s)	4.5 (1 H, t)	6.2 (2 H, d)	6.8–7.4 (24 H, m)
4-F	190–191		4.5 (1 H, t)	6.2 (2 H, d)	6.8–7.3 (24 H, m)
3-NO_2	165–166[a]		4.5 (1 H, t)	6.3 (2 H, d)	6.9–8.1 (24 H, m)
3,4-Cl_2	165–167		4.4 (1 H, t)	6.2 (2 H, d)	6.8–7.4 (24 H, m)
4-Me_2N	153–154	2.95 (6 H, s)	4.5 (1 H, t)	6.2 (2 H, d)	6.7–7.3 (24 H, m)

[a] Greenish yellow crystals; the other compounds are colorless.

Bond Dissociation Energies. Recently, we have developed a method of estimating bond dissociation energies (BDEs) from pK_{HA} and $E_{ox}(A^-)$ values using eq 7,[8] adapted from an equation derived by Nicholas and Arnold.[14]

$$\text{BDE} = 1.37pK_{HA} + 23.06E_{ox}(A^-) + 55.86 \qquad (7)$$

The $E_{ox}(A^-)$ values used in eq 7 are relative to the standard hydrogen electrode, which requires subtraction of 0.125 V from the $E_{ox}(A^-)$ values in Me_2SO given in Tables I and II. The constant, 55.86 kcal/mol, comes from a summation of values for the free energy of formation of the hydrogen atom in the gas phase, $\Delta G°_f(H)_g$, the free energy of solvation of the hydrogen atom, $\Delta G°_{sol}(H)$, the free energy of transfer of the proton from H_2O to Me_2SO, $\Delta G°_{tr}(H^+)$, and $T\Delta S°$. The BDEs calculated from eq 7 for cyclopentadienes and 1,4-pentadienes are summarized in Table III.

Examination of Table III shows that introduction of Ph substituents into the 2- and 5-positions of cyclopentadiene lowers the homolytic BDE of the acidic C–H bond by about 6 kcal/mol. Introduction of a 4-MeO or 4-Me group into one of the Ph rings causes a small additional decrease in BDE, whereas 3-MeO and 4-Cl substituents have no effect.[16] Note that the change in BDE parallels the change in pK_a for CpH_2 and 2,5-$(Ph)_2$-CpH_2, indicating parallel effects on homolytic and heterolytic C–H BDEs, but the introduction of the 4-MeO and 4-Me groups causes opposite effects because these groups stabilize radicals but destabilize anions.

The acidic C–H bonds in the tetra- and pentaphenylcyclopentadienes have lower homolytic BDEs than that in CpH_2 by 2–3 kcal/mol. Twisting of the phenyl groups in these polyphenylcyclopentadienes evidently reduces their effect, relative to the two Ph groups in 2,5-diphenylcyclopentadiene. This is the result of increased steric hindrance causing inhibition of a stereoelectronic effect in the radical, since phenyl substitution ordinarily decreases BDE. For example, the BDE for Ph_2CH_2 is over 5 kcal/mol less than that of toluene,[8] and the BDE estimated for 9-phenylfluorene is 5.5 kcal/mol lower than that of fluorene.[17] The BDE of Me_5-CpH is 4.1 kcal/mol lower than that of CpH_2. This decrease is due almost entirely to the effect of the methyl group at C-1, since an almost identical decrease in BDE (4.2 kcal/mol) is estimated for 9-methylfluorene compared with fluorene.[17]

The BDE value for the benzylic C–H bond in 1,1,3,5,5-pentaphenyl-1,4-pentadiene is 6 kcal/mol lower than that for cyclopentadiene and about 3 kcal/mol lower than that of its cyclic analogue 1,2,3,4,5-pentaphenylcyclopentadiene. The lower homolytic BDE for 1,1,3,5,5-pentaphenyl-1,4-pentadiene contrasts with the lower pK_a's for CpH_2 and Ph_5-CpH, by 5.4 and 10.9 units, respectively, which point to lower heterolytic C–H BDEs for the latter two. The comparison of the BDEs in Me_5-CpH and CpH_2 provides another example of this kind. Here the homolytic BDE for the acidic C–H bond in Me_5-CpH is 4 kcal/mol lower, but CpH_2 is a stronger acid by 11 kcal/mol.

The essential absence of substituent effects on the BDEs of the acidic C–H bonds in 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadiene was anticipated by the ΔAOP values, which are close to zero. The importance of orbital overlap in determining the size of BDEs is most evident for the 4-Me_2N substituent, which causes a 4 kcal/mol decrease in BDE in arylacetonitriles[17] but has no effect on the BDE of the benzylic C–H bond in 4-$Me_2NC_6H_4CH(CH{=}CPh_2)_2$ because twisting of the phenyl ring containing the Me_2N group precludes effective overlap.

Summary. The pK_a of cyclopentadiene (CpH_2) in Me_2SO estimated by the Breslow method, relative to triphenylmethane, has been brought into good accord with the value of 18 obtained by the indicator method by using the homolytic bond dissociation of 81 for Ph_3C–H, obtained by our acidity oxidation potential method, in place of the literature value of 75. The radical cation derived from cyclopentadiene is estimated to have a $pK_{HA^{\bullet+}}$ of −17 in Me_2SO. Its acidity is decreased to −8 by the presence of two phenyl groups, to −8.5 by the presence of five phenyl groups, and to −6.5 by the presence of five methyl groups. ($(Ph_2C{=}CH)_2CHPh$, an open-chain analogue of Ph_5CpH, is 11 pK_{HA} units less acidic, but the corresponding radical cation is 11.5 units more acidic than Ph_5-$CpH^{\bullet+}$. 4-$Me_2NC_6H_4CH(CH{=}CPh_2)_2^{\bullet+}$ is 13 units less acidic than its parent $C_6H_5CH(CH{=}CPh_2)_2^{\bullet+}$.

Experimental Section

Materials. Cyclopentadiene was prepared by cracking its dimer as described in the literature.[18] It was fractionally distilled twice and a fraction, bp 39 °C, was collected in a receiver cooled with dry ice. The CV measurements were carried out immediately after distillation on a fraction: ^1H NMR ($CDCl_3$) δ 2.97 (m, 2 H), 6.3–6.5 (m, 4 H).

1,1,3,5,5-Pentaphenyl-1,4-pentadiene was synthesized by the method of McEwen.[19] Crystallization from glacial acetic acid gave material, mp 172 °C (lit.[19] mp 172–173 °C). The 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes were synthesized and purified similarly (Table IV). Elemental C, H, and N analyses and mass spectral analyses for 3-[4-(dimethylamino)phenyl]-1,1,5,5-tetraphenylcyclopentadiene were satisfactory.

2,5-Diphenylcyclopentadiene and its 4-MeO, 4-Me, 3-MeO, and 4-Cl derivatives were a gift from Professor G. Pagani, University of Milan.

1,2,3,4-Tetraphenylcyclopentadiene was synthesized by the method of Cava and Narasimhan.[20]

1,2,3,4,5-Pentaphenylcyclopentadiene was synthesized by the method of Rio and Sanz.[21]

1,2,3,4,5-Pentamethylcyclopentadiene was a gift of Professor Tobin J. Marks.

Electrochemistry. Oxidation potentials equal to the peak oxidation current were measured by cyclic voltammetry with a Bioanalytical Systems instrument (West Lafayette, IN). The working and auxillary electrodes were Pt and the reference electrode was Ag/AgI. The measurements were carried out in Me_2SO solution with 0.1 M tetraethylammonium tetrafluoroborate electrolyte. The sweep rate was 100 mV/s (reproducible to >±10 mV) with a reversible ferrocene–ferrocenium redox couple at $E_{1/2}$ = 0.875 V used as a standard. Wave widths are recorded along with the potentials in Tables I and II. Further details may be found in the preceding paper in this series.[1b]

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

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[14] Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165–2179.

[15] Irreversible $E_{ox}(A^-)$ values are shifted to more positive potentials, relative to their reversible counterparts, because of kinetic effects. The size of these shifts is difficult to judge, but each 50-mV shift will cause a 1.15 kcal/mol decrease in the calculated BDE.

[16] ΔBDE values must mirror ΔAOP values because they both depend on differences in the summation of pK_{HA} and $E_{ox}(A^-)$. The ΔBDE values allow comparisons between different families, however, such as cyclopentadienes and 1,4-dienes.

[17] Calculated from the data in ref 11.

[18] Wilkinson, G. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. IV, p 433.

[19] McEwen, W. E.; Yee, T. T.; Liao, T.-K. *J. Org. Chem.* **1967**, *32*, 1947–1954.

[20] Cava, M. P.; Narasimhan, K. *J. Org. Chem.* **1969**, *34*, 3641–3642

[21] Rio, G.; Sanz, G. *Bull. Soc. Chim. Fr.* **1966**, *12*, 3775–3779.

J. Am. Chem. Soc. **1988**, *110*, 2877-2885

Registry No. $PhCH(CH{=}CPh_2)_2$ (radical cation), 113567-87-6; $4\text{-}Me_2NC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-88-7; $4\text{-}MeC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-89-8; $4\text{-}FC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-90-1; $3,4\text{-}Cl_2C_6H_3CH(CH{=}CPh_2)_2$ (radical cation), 113567-91-2; $3\text{-}O_2NC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-92-3; CpH_2 (radical cation), 76563-67-2; $2,5\text{-}Ph_2CpH_2$ (radical cation), 113567-81-0; $2\text{-}(4\text{-}MeOPh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-82-1; $2\text{-}(4\text{-}MePh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-83-2; $2\text{-}(3\text{-}MeOPh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-84-3; $2\text{-}(4\text{-}ClPh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-85-4; $2,3,4,5\text{-}Ph_4CpH_2$ (radical cation), 113626-32-7; $1,2,3,4,5\text{-}Ph_5CpH_2$ (radical cation), 113567-86-5; $1,2,3,4,5\text{-}Me_5CpH_2$ (radical cation), 91809-81-3.

Spectroscopic and Kinetic Characteristics of Aroyloxyl Radicals. 1. The 4-Methoxybenzoyloxyl Radical[1]

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Abstract: A detailed analysis of the time-resolved, UV-visible spectrum obtained by 308-nm laser flash photolysis of bis(4-methoxybenzoyl) peroxide proves that the broad, structureless absorption in the 500–800-nm region is due to the 4-methoxybenzoyloxyl radical. This radical also has an absorption at 320 nm. The long-wavelength absorption, for which there is less interference from other light-absorbing transients, has been used to measure absolute rate constants, k, for the reaction of 4-methoxybenzoyloxyl with a wide variety of organic substrates at ambient temperatures, e.g., cyclohexane, benzene, triethylsilane, cyclohexene, and 1,3-cyclohexadiene for which k in CCl_4 = $(5.3 \pm 3.0) \times 10^5$, $(2.3 \pm 0.2) \times 10^6$, $(4.8 \pm 0.1) \times 10^6$, $(6.4 \pm 0.3) \times 10^7$, and $(4.8 \pm 0.2) \times 10^8$ M^{-1} s^{-1}, respectively. Compared with the *tert*-butoxyl radical the 4-methoxybenzoyloxyl radical is about as reactive in hydrogen atom abstractions but is very much more reactive in additions to multiple bonds. The rate constant for decarboxylation of 4-methoxybenzoyloxyl at 24 °C is $(3.4 \pm 0.1) \times 10^5$ s^{-1} in CCl_4 but is reduced to $\leq 2 \times 10^4$ s^{-1} in CH_3CN. The 4-methoxybenzoyloxyl radical can also be photodecarboxylated by using 700-nm light from a second laser or by using high power levels in the primary laser.

The widespread use of benzoyl peroxide to initiate free-radical chain reactions in solution has resulted in numerous mechanistic investigations of its decomposition and of the decomposition of other diaroyl peroxides.[3] There can be no doubt that the thermal decomposition of these peroxides yields the corresponding aroyloxyl radicals.

$$ArC(O)OOC(O)Ar \xrightarrow{\Delta} 2ArCO_2^{\bullet} \qquad (1)$$

These radicals may decarboxylate

$$ArCO_2^{\bullet} \rightarrow Ar^{\bullet} + CO_2 \qquad (2)$$

or react with the solvent or some added substrate by, for example, a hydrogen atom abstraction

$$ArCO_2^{\bullet} + RH \rightarrow ArCO_2H + R^{\bullet} \qquad (3)$$

and/or an addition

$$ArCO_2^{\bullet} + RH \rightarrow ArCO_2\dot{R}H \qquad (4)$$

Studies of the competition between reaction 2 and reaction 3 (and/or reaction 4) have yielded a wealth of relative rate data but no absolute rate constants.[4]

Kinetic measurements on aroyloxyl radicals have, until very recently, been confined to CIDNP investigations of the benzoyloxyl radical.[5-9] The CIDNP results provide "direct" support for a rather surprising conclusion that was first drawn by Bevington and Lewis[10] nearly 30 years ago. These workers used ^{14}C-labeled diaroyl peroxides and chemical trapping with styrene. Whereas the thermal decomposition of diaroyl peroxides gave only aroyloxyl radicals, the photodecomposition generated some aryl radicals, indicating either that some of the aroyloxyl radicals were formed in an electronically excited state or that an electronically excited peroxide molecule could dissociate to aryl radicals.

$$ArC(O)OOC(O)Ar \xrightarrow{h\nu} 2(1 - f)ArCO_2^{\bullet} + 2fAr^{\bullet} + 2fCO_2 \qquad (5)$$

At 25 °C benzoyl peroxide had an f value of 0.29 and bis(4-methoxybenzoyl) peroxide an f value of 0.07.[10] Evidence was also obtained that those aroyloxyl radicals that survived photodissociation behaved in the same way as the thermally generated radicals.[10] The CIDNP studies on $C_6H_5CO_2^{\bullet}$ radicals using various peroxide precursors have yielded $k_2 \sim 1 \times 10^8$ s^{-1} at 130 °C,[5] at 100 °C,[6] and at 90 °C[9] for thermally generated radicals; $k_2 > 10^{10}$ s^{-1} at room temperature for radicals generated by direct photolysis;[9] and intermediate k_2 values for radicals generated by photosensitized decomposition.[8]

Product studies associated with the CIDNP work[8,9] and by several other research groups[11-13] have all supported Bevington and Lewis' original conclusion[10] that at least some of the benzoyloxyl radicals formed by direct photolysis of appropriate peroxides,[7-13] and to a lesser extent by photosensitized processes,[8,11] undergo decarboxylation much more rapidly than is the case when they are formed thermally. There is also evidence that the direct photolysis of *tert*-butyl perbenzoate gives a significantly higher

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[1] Issued as NRCC No. 28641.

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[3] Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957. Swern, D., Ed. *Organic Peroxides*; Wiley: New York, 1970, Vol. 1; 1971, Vol. 2; 1972, Vol. 3. Patai, S., Ed. *The Chemistry of Peroxides*; Wiley-Interscience: New York, 1983.

[4] For a comprehensive survey of kinetic data on benzoyloxyl and related radicals, see: Scaiano, J. C.; Howard, J. A. *In Landolt-Börnstein. New Series. Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Part d, pp 127–141. For some more recent measurements of relative rate constants for benzoyloxyl radical reactions, see, e.g.: Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1573–1588. Lane, J.; Tabner, B. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1823–1826.

[5] Schwerzel, R. E.; Lawler, R. G.; Evans, G. T. *Chem. Phys. Lett.* **1974**, *29*, 106–109.

[6] Den Hollander, J. A. *Chem. Phys.* **1975**, *10*, 167–184.

[7] Poranski, C. F., Jr.; Moniz, W. B.; Sojka, S. A. *J. Am. Chem. Soc.* **1975**, *97*, 4275–4283.

[8] Den Hollander, J. A.; Van Der Ploeg, J. P. M. *Tetrahedron* **1976**, *32*, 2433–2436.

[9] Nedelec, J. Y.; Lefort, D. *Tetrahedron* **1980**, *36*, 3199–3203.

[10] Bevington, J. C.; Lewis, T. D. *Trans. Faraday Soc.* **1958**, *54*, 1340–1344.

[11] Koenig, T.; Hoobler, J. A. *Tetrahedron Lett.* **1972**, 1803–1806.

[12] Kitamura, A.; Sakuragi, H.; Yoshida, M.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1393–1398.

[13] For a related study, see: Takahara, S.; Urano, T.; Kitamura, A. Sakuragi, H.; Kikuchi, O.; Yoshida, M.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 688–697.

0002-7863/88/1510-2877$01.50/0