Electron Spin Resonance Studies of Phenyl and Pyridyl Radicals in Aqueous Solution¹

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Publication costs assisted by Carnegie-Melion University and the U.S. Energy Research and Development Administration

ESR spectra of a number of phenyl and 2-pyridyl radicals have been detected in aqueous solution. Two methods of radical production were used, namely, reaction of SO_4 . produced by photolysis of $S_2O_8^{2-}$ with aromatic carboxylate ions and reaction of e_{aq}^{-} produced by radiolysis with aromatic bromides. Most radicals had only carboxyl groups as further substituents. The proton hyperfine constants of the phenyl radicals, $a_{\rm o} \sim 17$, $a_{\rm m} \sim 6$, and $a_{\rm p} \sim 2$ G, are readily assigned on the basis of effects of the various substitutions and agree well with previous determinations for radicals in the solid state. With four phenyl radicals containing two to four carboxyl groups it was also possible to detect all of the possible ¹³C containing isomers at natural abundance. A hyperfine constant of \sim 135 G for the carbon at the radical site confirms the σ nature of phenyl radical. The other ring ¹³C hyperfine constants are $a_0^{\text{C}} \sim 7.5$, $a_m^{\text{C}} \sim 13$, and $a_p^{\text{C}} \sim 1.5$ G. Both ¹⁴N and proton hyperfine constants were determined for the 2-pyridyl radicals. Only the ¹⁴N value $(\sim 27 \text{ G})$ was known previously. The g factors of phenyl and 2-pyridyl radicals are low (near or below the free electron value) reflecting their σ nature. The presence of carboxyl groups in a phenyl radical affects the g factor in an additive fashion with increments of 13, -2, and -3 units in the fifth decimal place for ortho, meta, and para substituents, respectively. The observation of phenyl and 2-pyridyl radicals demonstrates in a direct way that these radicals are formed in the two above-mentioned reactions. (One example each of a 4-pyridyl and a pyrazyl radical were also produced and studied.) Phenyl and 2-pyridyl radicals with no ortho carboxyl group were found to be very reactive toward addition to another aromatic molecule and were best detected using low concentrations $(5 \times 10^{-4} M)$ of aromatic bromide. Spectra of the unsubstituted phenyl and 2-pyridyl radicals were obtained in this way from the corresponding bromides. At higher solute concentrations such as used for the decarboxylation reactions these radicals react further to form adducts of the cyclohexadienyl type. Radicals with an ortho carboxyl group (for example, 2-carboxylphenyl radical produced from phthalate) are much less reactive toward addition and could be studied at higher concentrations of the starting compound. Reaction of SO4.- with acids in which three (or more) adjacent carboxyl groups are present leads preferentially to loss of a central or interior carboxyl group. To provide data for comparison with earlier indirect studies, a number of adducts of phenyl and pyridyl radicals to CH_2 — NO_2^- and trimesate were studied and their hyperfine constants determined. In the latter cases it was found that the ortho and meta protons in the phenyl radical which has added (i.e., the side group in the final cyclohexadienyl radical) can produce splittings of ~ 0.05 and ~ 0.3 G, respectively. The radicals detected in experiments in which SO4.- reacts with terephthalate and trimesate are thus shown to be adducts of phenyl type radicals to the starting molecule and not SO_4 . - adducts as previously suggested.

Introduction

The ESR spectra of phenyl radical²⁻⁶ and the related pyridyl radicals⁶⁻⁹ have been known for some time from studies in the solid phase. Indirect ESR evidence for the formation of phenyl radicals in aqueous solution has been found in studies of the reactions of reducing species with diazonium ions¹⁰ and of SO₄.- with benzoate¹¹ but no direct ESR observations of phenyl radicals in solution have been reported. In the present paper we wish to present ESR spectra for a number of phenyl, pyridyl, and pyrazyl radicals in aqueous solution as prepared by several types of reactions.

The present work was initiated because of a desire to explore further the reactions of SO_{4} .⁻ with aromatic compounds. The reactions of a number of oxidizing radicals are being used to probe enzyme deactivation¹² and it is important to understand in more detail the nature of the reactions. Norman et al.¹³ have reported that 1,3,5-benzenetricarboxylate (trimesate) and terephthalic acid form adducts with SO_{4} .⁻ while benzene yields the OH adduct¹³ and benzoate appears to be decarboxylated.¹¹ It was because of this

apparent variety of reactions that we began with $SO_{4^{-}}$ and aromatic acids. The results to be described help considerably in eliminating much of the previous confusion regarding these reactions.

Experimental Section

The radicals were prepared using previously described techniques by radiolysis directly in the ESR cavity with 2.8-MeV electrons¹⁴ or by photolysis with a 1-kW mercuryxenon lamp.¹⁵ Magnetic field measurements were made by means of a field-tracking NMR unit and frequency counter.¹⁴ The g factors were determined by reference to the peak from the irradiated silica cell in the radiolysis experiment or directly from field and microwave frequency measurements in the photolysis work. The estimates of experimental accuracy as given in footnote a, Table I are based on the reproducibility of splittings that occur several times in a given spectrum and upon comparisons of parameters from different spectra. The results refer to solutions within a few degrees of room temperature, about 24°. Most of the aromatic precursors were from the Aldrich Chemical Co.

Radical	Sub- stituent	Position ^b	Method °	$a_{2,6}^{H}$ (ortho)	$a_{3,5}^{H}$ (meta)	$a_4^{\mathrm{H}}\left(\mathrm{para}\right)$	g
I ^d	None	<u> </u>	eao	17.43 (2)	6.25(2)	2.04	2.00227
II	0 ⁻	3	ead	20.13, 15.77	9.12	1.32	2.00226
III	OH^{f}	4	e _{ac}	$(16.8)^{g}(2)$	4.90(2)		$(2.00226)^{g}$
IV	CO,	2	$e_{a_0}^{m}$, SO_4^{-}	18.11	$7.85, 5.87^{h}$	1.71	2.00240
v	co,-	4	e _{ao} -	17.06(2)	5.88(2)		2.00224
VI	CO ₂ -	2,6	SO_4		7.41(2)	1.39	2.00254
VII	CO,-	2, 5	e_{ao} , SO_4	18.71	7.66	1.44	2,00238
VIII	CO,-	2,4	e_{a0} , SO_4	17.66	7.45, 5.59 ^{h}		2.00237
IX	CO ₂ -	2, 3, 6	SO_4		7.47	1.17	2.00251
Х	CO ²	2, 4, 6	SO_4^{-1}		7.10(2)		2.00251
XI	CO ₂ -	2, 3, 5	SO4	18.14		1.23	2.00236
XII	CO ₂ -	2, 4, 5	SO_4^-	18.04	7.37		2.00237
XIII	CO_2^{-}	2, 3, 5, 6	SO4			0.95	2.00246
XIV	CO_2^{-}	2, 3, 4, 6	SO_4^-		7.43		2.00249
XV	CO_2^-	2, 3, 4, 5, 6	SO_4^-				2.00246

TABLE I: ESR Parameters of Phenyl Radicals^a

^a Hyperfine constants are given in gauss and are accurate to ± 0.03 G. The number of nuclei exhibiting the splitting are given in parentheses if different than one. The g factors were determined from field and frequency measurements in photolysis experiments and by reference to the peak from the silica cell in radiolysis experiments. Second-order corrections have been made. The relative values are believed accurate to ± 1 in the fifth decimal place and the absolute values to about ± 3 in the fifth place. ^b Positions are numbered according to

^c Radicals were produced by removal of Br⁻ from the appropriate bromide by reaction with e_{aq}^- (reaction 4) or by removal of a carboxyl group from the appropriate carboxylate ion by reaction with SO_4^- (reaction 1). ^{*d*} Values observed for this radical in an argon matrix are $a_o = 17.4$, $a_m = 5.9$, $a_p = 1.9$ G, g = 2.0023. ^{*e*} Observed at pH 12. If the pK of the radical is similar to that of phenol (9.9) then the OH proton should be dissociated at this pH. ^{*f*} Observed at pH 7. The OH proton should not be dissociated. ^{*g*} Only the high-field line group (a triplet) was observed because of CIDEP effects. ²² The *g* factor given in the table was assumed to allow determination of the ortho proton splitting. ^{*h*} As described in the text, the value of ~7.5 G can be assigned to the proton at the 3 position.

The 1,2,3- and 1,2,4-benzenetricarboxylic acids and benzenepentacarboxylic acid were from EGA-Chemie, KG (W. Germany), phthalic acid from Eastman Chemical Co., and bromobenzene and p-bromophenol from Baker. The samples of 1,2,3,5- and 1,2,3,4-benzenetetracarboxylic acids were kindly supplied by Dr. Klaus Eiben.¹⁶ The pH was adjusted with KOH, H₂SO₄, Na₂B₄O₇, Na₂HPO₄, and NaH₂PO₄ which were all Baker Analyzed Reagents. The Na₂S₂O₈ was obtained from Sigma Chemical Co. and *tert*butyl alcohol from Mallinckrodt.

Typical solutions used in the photolysis experiments contained 30-70 mM Na₂S₂O₈ and 1-5 mM of the aromatic acid. The pH was maintained with ~10 mM of the appropriate buffer (phosphate or borate) in the range 6-10. Flow rates varied from 5 to 40 cm³/min. Solutions for radiolysis experiments contained 0.5-5 mM of the desired compound (bromide) and were in the pH range 11-12. In most cases no other solute was present. Where an OH scavenger was needed, *tert*-butyl alcohol was used. Solutions were deoxygenated by bubbling with N₂ or N₂O.

Results and Discussion

Direct Observation of Phenyl and Related Radicals. Because the radicals produced by reaction of SO_{4} with terephthalate and 1,3,5-benzenetricarboxylate (trimesate) had already been reported,¹³ the initial experiments were carried out with phthalate, 1,2,4,5-benzenetetracarboxylate, and benzenepenta- and hexacarboxylates. Solutions containing these compounds and $S_2O_8^{2-}$ at pH 7-10 were photolyzed and new ESR spectra characterized by relatively low g factors were found. With phthalate only this set of lines with the parameters $a^{\rm H}$ (1) = 18.11, 7.85, 5.87, and 1.71 G, g = 2.00240 was present, while in the other cases a mixture of radicals occurred. The new spectra are ascribed to phenyl radicals formed by decarboxylation of the carboxylate ion by SO₄.⁻, (eq 1). The magnetic parameters are

$$\operatorname{ArCO}_2^- + \operatorname{SO}_4^- \to \operatorname{Ar}_2^+ + \operatorname{SO}_4^{2-} + \operatorname{CO}_2 \tag{1}$$

similar to those reported by Kasai et al.⁴ for phenyl radical itself in an argon matrix ($a_0 = 17.4$, $a_m = 5.9$, $a_p = 1.9$ G, g = 2.0023) with the low g factor reflecting the σ nature of the radical. As was mentioned in the Introduction, such a decarboxylation reaction has been demonstrated indirectly in the case of benzoate by observation of the phenyl adduct to CH2=NO2-.11 Phenyl radicals were also successfully produced in photolytic experiments with 1,2,3- and 1,2,4benzenètricarboxylates, 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-benzenetetracarboxylates, benzenepentacarboxylate, and benzenehexacarboxylate. The spectrum obtained with benzenepentacarboxylate is shown in Figure 1. ESR parameters for all phenyl radicals observed are summarized in Table I where they are also assigned an identifying Roman numeral. Further discussion of the magnitudes of the hyperfine constants is given in a later section. From the fact that no changes in the spectra assigned to phenyl radicals with carboxyl substituents occurred to pH 10 we assume the acid protons are dissociated as shown.

In each case the observed radicals can be identified as resulting from decarboxylation of the parent carboxylate. The proton hyperfine constants are assignable to specific positions by comparison with those for the unsubstituted radical. Thus in the case of phthalate (radical IV) there is one ortho proton, two meta protons, and one para proton. The 18.11- and 1.71-G splittings are correspondingly as-



Figure 1. Second-derivative ESR spectrum obtained upon photolysis of a solution of 5 m*M* benzenepentacarboxylic acid and 70 m*M* $Na_2S_2O_8$ at pH 6.7 (phosphate buffer). The main intensity is from the phenyl radicals XIII and XIV formed by loss of an "internal" carboxyl group. Weak lines are observed from phenyl radical X which is produced in secondary reactions. Spectrum A is attributed to the pentacarboxyphenoxyl radicals with single ring protons in the meta, ortho, and para positions, respectively. Spectrum B may come from the ortho or para tetracarboxybenzosemiquinone ion. Spectra F and G are hydroxycyclohexadienyl radicals formed by OH addition to the unsubstituted position in benzenepentacarboxylate and 1,2,3,5-benzenete-tracarboxylate.

signed to the ortho and para protons while the 7.85- and 5.87-G values must belong to the meta protons. In a number of other cases more than one radical can be produced but the pattern of splittings allows identification. With 1,2,3-benzenetricarboxylate two radicals are possible but only VI produced by loss of the central carboxyl group is found. Similarly the two radicals XIII and XIV resulting from the loss of an internal carboxyl group from benzenepentacarboxylate were found with no trace of the third radical which would result from loss adjacent to the unsubstituted position. With 1,2,3,5-benzenetetracarboxylate the main intensity is from radical X caused by loss of the carboxyl group at position 2 and only weak lines of radical XI formed by loss at positions 1 or 3 occur at \sim 1% of the intensity of those of the previous radical (see Figure 2). No evidence was found for loss of the carboxyl group at the 5 position. Again loss of a central carboxyl group is preferred. (With 1,2,4-benzenetricarboxylate only the phenyl radicals produced by loss of carboxyl groups at positions 1 (VIII) or 2 (VII) are observed but loss at the 4 position also occurs and leads to an adduct to another molecule as will be discussed in the next section.) The high degree of selectivity for loss of a particular carboxyl group can be interpreted as demonstrating oxidation by SO_4 .⁻ of the molecule as a whole followed by loss of the most labile CO₂ group rather than attack of SO_4 .⁻ at a particular site.

No lines attributable to phenyl radicals were found for benzoate, isophthalate, terephthalate, and trimesate. In the latter two cases, spectra of radicals identifiable as of the cyclohexadienyl type as reported by Norman et al.¹³ were obtained. These spectra will be discussed in more detail in the next section. Similar radicals were detected for 1,2,4-benzenetricarboxylate in addition to the phenyl radicals VII and VIII. With benzoate and isophthalate only weak lines which could not be analyzed were detected.

The spectra obtained with all of the compounds yielding phenyl radicals (with the exception of phthalate) were complex to varying degrees in that lines from other types of radicals were also present. These complex spectra were analyzed by grouping together the lines with similar intensity



Figure 2. A portion, recorded at high gain, of the spectrum obtained upon photolysis of a solution of 2 m*M* 1,2,3,5-benzenetetracarboxylate and 60 m*M* Na₂S₂O₈ at pH 7.3. The off-scale peak is the highfield line of the 7.10-G triplet of 2,4,6-tricarboxyphenyl radical. Lines corresponding to radicals containing ¹³C are labeled with the position of that atom according to the scheme used in Table II. (The primes represent the carboxyl carbons.) Weak lines of phenyl radical XI formed by loss of a carboxyl group at the 1 or 3 positions are also observed as are lines from the hydroxycyclohexadienyl radicals produced by OH addition to the tetracarboxylate (B) and to trimesate (A).

and a common spectral center and then looking for acceptable patterns of splitting. All of the spectra for which parameters are reported in the tables were identified by means of most, if not all, of the lines and are known with a high degree of certainty. The radicals responsible for the additional lines could be identified as of the hydroxycyclohexadienyl, phenoxyl, and semiquinone ion types. The intensity of these spectra depended upon pH, flow rate, and reactant concentration becoming more intense at higher pH, lower flow rate, and lower concentration. Hydroxycyclohexadienyl radicals were identified by the \sim 30-G proton splitting by the CHOH ring proton and the parameters were checked against results of studies specifically of this type of radical.^{17,18} These radicals can be formed at pH >10 as a result of the conversion of SO₄-⁻ to OH by

$$SO_4 - + OH^- \rightarrow OH + SO_4^{2-}$$
 (2)

with a rate constant of $6.5 \times 10^7 M^{-1} \sec^{-1.19}$ At lower pH values (7-9), this reaction cannot be significant and some other mechanism must exist for producing hydroxycyclohexadienyl radicals. From the fact that the lines of these radicals are less intense at higher solute concentrations it seems likely that the reaction of SO₄.- with water (eq 3) is

$$SO_4 - H_2O \to OH + H^+ + SO_4^{2-}$$
 (3)

a source of OH which subsequently adds to the aromatic. The rate constant for this reaction has been reported to be $10^3-10^4 \sec^{-1} 1^{9,20}$ which is sufficiently fast to contribute. The phenoxyl and semiquinone ion radicals are probably secondary products and were identified by the high g factors and by reference to the parameters reported for a number of such radicals²¹ (some of which were also observed in this study).

The spectrum obtained with benzenepentacarboxylate and given in Figure 1 illustrates the large number of radicals possible. In addition to lines of the two main phenyl radicals there are lines from the phenyl radical X, two hydroxycyclohexadienyl types, from four radicals which can reasonably be identified as of the phenoxyl type, and from one semiquinone ion. (See the figure caption for the identi-

The Journal of Physical Chemistry, Vol. 79, No. 14, 1975

fication.) At higher gain it was possible to observe lines from the ¹³C containing phenyl radicals (XIII, XIV) and weak lines of the phenyl radical XII and the OH adduct to 1,2,4,5-benzenetetracarboxylate. Exactly the same spectrum was observed from a sample of the pentacarboxylic acid which had been recrystallized and which showed no impurities in experiments¹⁸ which allowed observation of the ¹³C containing OH adduct. The two minor phenyl radicals, two of the hydroxycyclohexadienyl radicals, and three of the phenoxyl radicals each appear to be produced from acids with one less carboxyl group than the starting compound. Somewhat similar behavior was found for benzenehexacarboxylate and 1,2,3,5-benzenetetracarboxylate. With the former compound both major phenyl radicals, the OH adduct, and the phenoxyl radical produced from the pentacarboxylate were observed as well as three phenoxyl radicals with only four carboxyl groups. With the 1,2,3,5-tetracarboxylate the OH adduct to trimesate was observed (as shown in Figure 2) as was the 2,4,6-tricarboxyphenoxyl radical. These radicals formed from compounds with one carboxyl group less than the starting compound must originate in secondary processes and not from impurities. This argument is supported by the fact that the radicals of concern are more prominent at lower flow rates. From the appearance of phenyl and hydroxycyclohexadienyl radicals as well as the phenoxyl radicals it is clear that there must be some source of the acids themselves. One possibility is that the bimolecular disappearance of at least the highly substituted phenyl radicals proceeds by an electronic disproportionation which yields a positive and negative ion and ultimately, after reaction with water, the corresponding substituted benzene and phenol.

A common feature of all of the phenyl radicals produced by reaction of SO_4 .⁻ is a carboxyl group ortho to the radical site. It is clear that such a structure must stabilize the radical against further reaction such as addition to another ring. If this conclusion is correct then the same radicals should be observable when produced by other routes such as the reaction of e_{aq}^- with phenyl bromides. This type of reaction does indeed occur and in radiolytic experiments (eq 4) with o-bromobenzoate, 2-bromoterephthalate, and

$$ArBr + e_{aq}^{-} \rightarrow Ar \cdot + Br^{-}$$
(4)

4-bromoisophthalate, the spectra of radicals IV, VII, and VIII were readily observed. Although no OH scavenger was employed in these experiments no other radicals were observed. Apparently adducts of OH to the bromo compounds did not give sufficient intensity to be detected. It is important to note that in each case the spectrum is identical with that obtained by SO_4 -reaction with the appropriate acid.

This same reaction also allowed observation of the unsubstituted phenyl radical from bromobenzene as well as the phenyl radicals II, III, and V from *p*-bromophenol, *m*bromophenol, and *p*-bromobenzoate. In these three cases the concentration of the aromatic compound was kept low to prevent addition of the phenyl radical to a second molecule. The optimum concentration of the halide was about $5 \times 10^{-4} M$ with both higher and lower concentrations giving less signal. Such a low concentration can be used because of the high rate constant for reaction with e_{aq}^{-} . The presence of up to 10 m*M tert*-butyl alcohol as an OH scavenger had little effect on signal intensity although 50 m*M* decreased the signals by about a factor of 2. Apparently, at this concentration the reaction of the phenyl radical with *tert*- butyl alcohol becomes important. The spectra of these radicals showed a strong intensity anomaly as the result of $CIDEP^{22}$ with the low-field lines weak and inverted. This fact shows that a major disappearance pathway under these conditions is by radical-radical reaction.

The intensity of the spectra of the phenyl radicals increased markedly in going to the more highly substituted compounds as a result of slower radical-radical reactions for these multiply charged radicals as well as the simpler spectra. The intensity was so great with 1,2,3-benzenetricarboxylate, 1,2,3,5-benzenetetracarboxylate, and benzenepentacarboxylate that lines from the naturally occurring ¹³C containing phenyl radicals could be observed. With the latter compound both phenyl radicals could be studied. In each case all of the possible ¹³C hyperfine constants could be determined. The values are given in Table II.

Figure 2 illustrates some of the lines for the ¹³C containing radicals in the case of 1,2,3,5-benzenetetracarboxylate. Shown here is the region around the high-field line of the 1:2:1 triplet for the ¹²C form. Both of the lines in the pairs split around the ¹²C line are evident for the three smallest ¹³C hyperfine constants (0.73, 1.77, and 2.13 G). The peak heights are, starting with the smallest splitting, 0.5, 0.5, and 1% of that of the ¹²C radical. Only the high-field satellite is evident for the radicals with the 7.08- and 13.06-G constants but in the latter case the high-field satellite of the central line of the 1:2:1 triplet is also in the portion shown. The lines for the radical with ¹³C at the radical site $(a^{C} = 137.1 \text{ G})$ are far away and are not shown. Also evident in this figure are lines from radical XI formed by loss of a carboxyl group from the 1 or 3 position and OH adducts to 1,2,3,5-benzenetetracarboxylate (A) and to trimesate (B).

Assignment of the hyperfine constants of the ring carbons was made by reference to the INDO calculations²³ (see Table II). In each radical a large splitting of ~ 135 G occurs which is assigned to the carbon atom at the radical site. The relative intensities of the other lines with the various ${}^{13}C$ splittings (0.5% of the ${}^{12}C$ species for one carbon atom per radical or 1% for two equivalent atoms) together with the pattern which occurs upon changing the position of the carboxyl groups allows all of the other values to be assigned with reasonable certainty. The splittings assigned to ortho, meta, and para positions remain quite constant for the four radicals as is found for the proton splittings. A similar behavior is found for the splittings assigned to the carboxyl carbons and the assignment is quite certain except in the case of radical XIV where it is possible that the 1.58- and 2.10-G splittings could be reversed. The existence of ~0.7-G splittings only for radicals X and XIV assures that this value belongs to the para carboxyl carbon.

Similar reactions could be carried out with several pyridine and pyrazine derivatives. Thus the 2-pyridyl radical (XVI, see Table III) could be produced from 2-bromopyridine and the radicals XVII-XXI could be produced from the appropriate carboxylic acids. As with the benzenecarboxylic acids there occurred lines of other radicals in some of these spectra which could be assigned to OH adducts (by means of the large proton splitting at the attachment site) and phenoxyl or semiquinone ion radicals (by means of high g factors and small splittings). The proton hyperfine constants of XVI-XIX were assigned to the specific positions by noting the effects of changing the position of substitution. Those of XX and XXI could be assigned by reference to the phenyl and 2-pyridyl radicals, respectively.

		Hyperfine constants ^b								
Radical	Carboxyl position	1	2,6	3,5	4	2',6'	3′,5′	4'		
VI	2.6	135.31	7,42(2)	12.56(2)	1.27	1.57 (2)				
x	2, 4, 6	137.15	7.08(2)	13.06(2)	1.77	2.13(2)		0.73		
XIII	2, 3, 5, 6	132.93	7.64(2)	12.78(2)	1.54	1.42(2)	4.42(2)			
XIV	2, 3, 4, 6	135.55	7.76	12.88	1.58	2.90	4.06	0.70		
	-, -, -, -		6.94	12.28		2.10				
I (INDO)°	None	151.3	-4.8	10.7	-2.6					

^a Values in gauss. The number of nuclei displaying the splitting are given in parentheses if different than one. ^b Unprimed positions are numbered as in Table I (see footnote b). Primed numbers refer to the carboxyl carbon at the corresponding position. ^c Values calculated by the INDO method as given by Pople et al.²³

FABLE III: ESR Parameters of Pyridyl and Pyrazyl Radicals ^a								
F	ladical	Method ^b	a ^N	<i>a</i> ₃ ^H	$a_4^{ ext{ H}}$	a ₅ ^H	- <i>a</i> ₆ ^H	g
XVI		eaq	26.95	1.28	4.12	8.56	4.99	2.00202
XVII	O_{a}	SO_4	27.73	1.56	3.70	9.68		2.00219
XVIII	O.C.	SO_4	27.58	1.48		8.08	4.84	2.00207
XIX	-0.C N.	SO_4	28.84		4.09	8.24	4.43	2.00206
XX	$ \frac{1}{5} \underbrace{\bigcup_{i=1}^{i}}_{V} \underbrace{CO_2}_{i} $	SO_4	0.95	9.99°		8.16 ^c	18.94	2.00245
XXI		\mathbf{SO}_4	28.38 (o) 0.27 (m)	2.39	7.32			2.00232

^a Hyperfine constants in gauss, see footnote a, Table I. ^b See footnote c, Table I. ^c These values were assumed to show the same asymmetry as is apparent for some of the phenyl radicals in Table I.

Decarboxylation could potentially occur at two sites in the cases of 2,3-, 2,5-, and 3,4-pyridinedicarboxylates but only the product radicals XVII, XVIII, and XX, respectively, were observed. Thus no spectrum of a 3-pyridyl radical was obtained. With 3,5-pyridinedicarboxylate a 3-pyridyl radical was formed but added to another molecule to form an adduct such as that observed with terephthalate. (This radical will be discussed in the next section.)

Indirect Detection of Phenyl Radicals. The observation of decarboxylation in the many cases discussed in the previous section suggests that this reaction occurs generally with all benzene carboxylates. In support of this idea, Gilbert et al.¹¹ have already observed such a reaction with benzoate by use of nitromethane trapping. Further experiments of this type were carried out here. The spectrum obtained with phthalate and nitromethane and showing lines of the adduct of o-carboxyphenyl to nitromethane (radical XXVI) is illustrated in Figure 3. The results are summarized in Table IV. Phenyl radicals were prepared either by reaction of SO_4 . with a carboxylate or e_{aq} with a bromide. In several instances both methods were used to prepare a given phenyl radical and the same adduct was found. Several cases are included in which the phenyl radical has been detected directly as described in the previous section. These various arguments together with the observation that the parameters of the adducts are all quite similar establish the radicals in Table IV very clearly as adducts of phenyl type radicals. In most cases, the lines of the adducts were wider than is usually encountered with simpler adducts suggesting unresolved hyperfine structure. The parameters for the phenyl adduct (XXII) agree with those reported by Gilbert et al.¹¹

Lines from three other adducts are evident in Figure 3. Two of these spectra, A and C, are known to arise from the attack of SO_4^- on nitromethane. Spectrum A is that of the dinitroethane radical anion produced by trapping of $\dot{C}H_2NO_2^{24,25}$ and spectrum C with the parameters $a^N =$ 23.62, $a^{H} = 7.15$ G, and g = 2.00504 is that assigned to the SO₄⁻ adduct to nitromethane.²⁶ Spectrum B with the approximate parameters $a^{N} = 23.7$, $a^{H} = 7.3$, and g = 2.0051seems to belong to a radical analogous to that observed by Gilbert et al.¹¹ and identified by them as the adduct of $C_6H_5CO_2$. Adducts with similar parameters were also found in experiments with benzoate and terephthalate. The parameters for these adducts, which are similar to those of the SO_4 - adduct in having a small nitrogen splitting of about 23.5 G, cannot be determined accurately in our spectra because of overlap of those lines with other lines in the

Radical	Substituent on phenyl	Position	Method ^{b, c}	a ^N	$a^{\mathrm{H}}(\mathrm{CH}_2)$	g
XXII	None		e_{aa} , SO_4	25.87	9.38	2.00494
XXIII	0-	2	ead	25.65	10.34	2,00501
XXIV	0"	3	e _{ad} -	25.67	9.47	2.00494
XXV	0-	4	e _{ad} -	26.10	9.60	2.00497
XXVI	CO_2^-	2	e_{an} , SO_4	25.68	9.97	2,00498
XXVII	CO_2^-	3	SO_4	25.91	9.42	2.00495
XXVIII	CO_2^{-}	4	e, SO4	25.87	9.28	2.00497
VVIV	<u>- ^</u>	35	sô.	25 94	0.73	2 00405

TABLE IV: ESK Parameters of Phenyl Radical Adducts to CH ₂	=NO ₂ ^{-u}
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^a Hyperfine constants in gauss, see footnote *a*, Table I. ^b Method of production of the phenyl or pyridyl radical, see footnote *c*, Table I. ^c For radiolysis experiments starting with e_{aq}^{-} the solutions contained 1 mM each of the bromide and nitromethane at pH 11. For photolysis experiments with SO₄⁻ the solutions contained 3 mM of the carboxylate, 3 mM of nitromethane, and 70 mM Na₂S₂O₈ at pH 9-10.5.



Figure 3. The low-field third of the ESR spectrum produced by photolysis of a solution containing 3 m*M* phthalate, 3 m*M* CH₃NO₂, and 70 m*M* Na₂S₂O₈ at pH 10.5 and showing lines of the adduct of *o*-carboxyphenyl radical to CH₂—NO₂⁻ (XXVI). Other lines are from the adducts of \cdot CH₂NO₂ (spectrum A), SO₄ \cdot ⁻ (C), and what is believed to be o-C₆H₄(CO₂⁻)CO₂ \cdot (B).

spectra. We agree that these adducts are probably formed from radicals of the type $C_6H_5C\dot{O}_2$.

The data of Table IV show that phenyl radicals are produced from terephthalate, isophthalate, and trimesate even though those radicals could not be observed directly. An experiment to reexamine the reactions of SO_4 . with terephthalate and trimesate gave spectra typical of cyclohexadienvl radicals which matched those reported by Norman et al.¹³ except that small triplet splittings (not previously reported) of 0.29 and 0.05 G, respectively, were found. In these cases the radicals cannot be SO_4^- adducts because all protons are accounted for without considering the small triplets. It is clear now that these radicals must be the adducts of p-carboxy- and 3,5-dicarboxyphenyl radicals to a parent molecule. Further proof of this idea is provided by experiments using mixtures with two different carboxylates. A photolysis experiment with 3 mM terephthalate and 1 mM trimesate showed clearly the presence of the four possible radicals produced by addition of the two phe-

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nyl types to the two starting compounds (i.e., radicals XXXIV, XXXIII, and XXXV in Table V and the adduct of 3,5-dicarboxyphenyl to terephthalate). Considerable spectral overlap occurs because adducts to the same carboxylate ion produce similar spectra and so it was not possible to get a complete analysis of this spectrum. Only the parameters of radical XXXIII could be accurately determined from this spectrum while those of XXXIV and XXXV are known from experiments on terephthalate and trimesate alone. No parameters for the fourth radical (with the weakest spectrum) were determined. Parameters for some other adducts of this type are shown in Table V. Experiments in which radicals were added to trimesate gave the best intensity. The radicals XXXVIII and XXXIX show that radicals of the 2- and 3-pyridyl type (produced from the appropriate bromides) also add to trimesate. Radical XL obtained in experiments with SO₄.- and 3,5-pyridinedicarboxylate shows that a radical of the 3-pyridyl type can be produced in this way but that it is reactive toward addition so only the adduct is observed.

The parameters for phenyl radical adducts in Table V are very similar to those reported by Beckwith and Norman¹⁰ who formed the initial phenyl radicals by reducing diazonium ions. In the one case where the same radical is reported (XXXIII) in both studies the parameters agree within experimental error (including the 0.29-G triplet). As mentioned above the parameters for radicals XXXV and XXXIV (see in Table V) formed in solutions of terephthalate and trimesate, respectively, agree (except for the smallest splittings) with those assigned by Norman et al.¹³ to SO₄.⁻ adducts. On the basis of the present work there is no evidence in any case for formation of an SO₄.⁻ adduct.

The origin of the ~ 0.3 -G splitting in phenyl adducts is demonstrated very clearly by the portions of spectra shown in Figure 4. Here phenyl radicals with zero, one, and two meta protons formed by decarboxylation of trimesate, isophthalate, and benzoate, respectively, have added to trimesate to produce radicals XXXIV, XXXII, and XXXI with a singlet (at this level of resolution) and doublet and triplet splittings of about 0.3 G. This result illustrates very graphically that the meta protons are responsible for this split-

TABLE V: ESR Parameters of Phenyl Radical Adducts to Aromatic Acids^{a,b}



Radical	Substituent	Position	<i>a</i> ₂ ^H	a3 ^H	a_4^{H}	a 5 ^H	a_6^{H}	a2', 6', H	a3,5, ^H	g
XXXI	CO ₂ -	1, 3, 5	2.52		2.52		31.52		0.29(2)	2.00317
XXXII	CO_2^{-}	1, 3, 5, 3'	2.52		2.52		31.78		0,28	2.00317
XXXIII°	CO2	1, 3, 5, 4'	2.52		2.52		31.66		0.29(2)	2.00318
$XXXIV^d$	CO2	1, 3, 5, 3', 5'	2.52		2.52		31.95	0.05(2)		2.00317
XXXV ^e	CO_2^-	1, 4, 4'	2.86	12.49		7.88	37.01		0.29(2)	2.00277
XXXVI	CO_2	1,3,3′	2.67^{f}		2.20^{f}	7.78	36.80		0.28	2.00305
XXXVII ^g	CO ₂ ; OH	1, 3, 5; 3'	2.52		2.52		31.23		0.34	2.00319
XXXVIII ^h	-O,C CO,		2.47		2.47		34.17			2.00311
XXXIX ^h			2.48		2.48		31.83			2.00312
XL			1.39 ^f		2.82^{f}		37.37	$a_1^{N} = 4.06$		2.00349

^a Hyperfine constants in gauss. see footnote *a*, Table I. ^b Except where noted phenyl radicals were produced in photolytic experiments from SO_4^- . Typical solutions contained 1–5 mM of the acid or acids and 30–70 mM Na₂S₂O₈ at pH 7–9. ^c Hyperfine constants reported for this radical by Beckwith and Norman¹⁰ are 32.0, 2.55(2), and 0.25(2) G. They prepared the initial phenyl radical by reduction of the diazonium ion. ^d Hyperfine constants reported by Norman et al.¹³ are 31.8 and 2.55(2) G. The initial phenyl radical was prepared by reaction of trimesate with SO₄⁻ as was done here but the final radical was incorrectly identified as the SO₄⁻ adduct to trimesate. ^e Hyperfine constants reported by Norman et al.¹³ are 36.8, 12.5, 7.9, 2.8 G. The 0.29(2) G splitting was not resolved and the radical was incorrectly identified as the SO₄⁻ adduct to trimesate. ^e Hyperfine constants the SO₄⁻ adduct to terephthalate. ^f These two proton splittings were assigned to specific positions under the assumption that the asymmetry is similar to that found in hydroxycylohexadienyl radicals.¹⁸ The alternative assignment with these two values interchanged is possible. ^g The *p*-hydroxyphenyl radical was produced at pH 9 by reaction of eaq⁻ with *p*-bromophenol. ^h Pyridyl radicals were produced by reaction of eaq⁻ with the appropriate bromides at pH 11.7.

ting. The further very small triplet splitting of 0.05 G in the case of radical XXXIV, where no meta protons are present, shows the magnitude of the splitting by ortho protons. All of the radicals in Table V follow this rule for the 0.3-G splitting with the exception of XXXVIII for which this splitting could not be resolved. (The lines were correspondingly broad, however.) With 1,2,4-benzenetricarboxy-late a spectrum of eight line groups corresponding to an adduct (or adducts) at the 5 position was observed in addition to the two phenyl radicals VII and VIII. Based on the reactivity observed for phenyl radicals with no ortho carboxyl group it is expected that decarboxylation at the 4 position will produce a radical which can add to another molecule. This adduct is presumed to be



Addition at the 5 position is shown by the presence of an ortho (8 G) and a meta (2.5 G) splitting in the adduct. The eight line groups are complex but can be interpreted as arising from two radicals with common major parameters of $a^{\rm H} = 37.58$, $a^{\rm H} = 7.30$, $a^{\rm H} = 2.80$ G, and g = 2.00302 but with two small additional splittings each of 0.21 and 0.15 and 0.46 and 0.20 G. The radical with splittings of 0.21 and 0.15 G is present at roughly three times the intensity of the other form. The presence of other unidentified weak lines

caused the eight line groups to be somewhat dissimilar in appearance. To explain the existence of two very similar radicals it is necessary to invoke two isomers with restricted rotation about the bond between the two rings. Such behavior has been proposed previously by Beckwith and Norman¹⁰ for the o-chlorophenyl adduct to trimesate but in that case a large difference in the methylene splitting of the two isomers was observed contrary to the present example. The small splittings in our spectrum are different than the rather uniform value of ~0.3 G assigned to the meta protons in Table V and if the radical structure is indeed as suggested then it must be concluded that the ortho splittings in the secondary ring can be as large as 0.15–0.20 G in certain instances.

Discussion of the Hyperfine Constants

The proton hyperfine constants found here for phenyl radical agree very well with those reported by Kasai et al.⁴ for the radical in an argon matrix. The values also agree with those calculated by the INDO method²³ for the σ structure ($a_o = 18.7$, $a_m = 6.1$, $a_p = 3.9$ G) with the calculated value for a_p about twice that observed. The assignment to specific positions is completely supported by the pattern of splittings for the various substituted radicals in Table I. In each case the splittings of the remaining protons are similar to those in the unsubstituted radical. The largest deviations are for radical II in which the presence of

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Figure 4. The high-field halves of the ESR spectra of the cyclohexadienyl-type radicals produced by trapping several phenyl radicals with trimesate. The three radicals trapped are given on the left and were obtained in experiments with trimesate itself and in mixtures with isophthalate and benzoate. In each case the major structure of the spectrum is the same with one large doublet splitting of ~32 G and a triplet of 2.52 G both from the protons on the cyclohexadienyl ring. The structure on the next finer scale of (from top to bottom) singlet, doublet, and triplet clearly is caused by the meta protons in the added radicals (illustrated). At higher resolution (lower microesate itself appear as 0.05-G triplets as shown above the upper trace. This further splitting must come from the ortho protons.

the meta O⁻ group introduces asymmetry into the ortho splittings and raises the value of a^{m} to 9.12 G. A similar asymmetry is seen for radical IV and it is possible to conclude by comparison of the values for IV, V, VI, and VII, for example, that the presence of an ortho carboxyl group raises the splitting by the meta proton on the same side of the ring to about 7.5 G. The splitting by the meta proton on the other side of the ring is affected very little.

The g factors of the radicals in Table I vary in a systematic fashion. A comparison of the values shows that carboxyl groups in ortho, meta, and para positions change the value by ± 13 , -2, and -3 units in the fifth decimal place, respectively, and that the effects are additive. The root mean square of the deviations between the measured values and those calculated using these increments and a value of 2.00227 (as observed) for the unsubstituted radical is 1.1 units in the fifth decimal place. Because of the σ character of the radical, which localizes the unpaired electron at the radical site, only a carboxyl group near the radical site (ortho position) can participate significantly in the singly occupied orbital and thereby shift the g factor.

The ¹³C hyperfine constants in Table II were assigned to specific ring positions by reference to the INDO calculations of Pople et al.²³ for unsubstituted phenyl radical (also included in the table for reference). The values for the carboxyl carbons were assigned by means of the intensities and pattern of splittings obtained upon changing the position and number of substituent carboxyl groups. The largest splitting of ~135 G is clearly that of the carbon at the radical site and the large magnitude demonstrates the σ na-

ture of phenyl radical (i.e., that a direct carbon 2s contribution to the singly occupied orbital is present to the extent of about 12%). The values found here agree with those determined for phenyl radical itself as prepared in the solid on silica gel (about $140 \text{ G})^5$ and by a deposition method in solid benzene (129 G)⁶ thus confirming the interpretation of those solid state spectra in terms of the large ¹³C hyperfine constant. The splittings of 7 and 13 G found here for two carbons each correspond well with the ortho and meta values predicted by calculation. The para values of 1.3-1.7 G are somewhat smaller than the predicted 4.8 G. Unfortunately INDO calculations give little help with a "mechanistic" interpretation of the origin of these latter ¹³C interactions and so cannot supply much insight into why the magnitudes of the ¹³C splittings at ortho and meta positions are reversed from the proton splittings. Because of the σ nature of the radicals it is difficult to anticipate the size of the splittings by the carboxyl carbons but values smaller than those of the carbons to which the carboxyl groups are attached seem likely. The values found conform to this idea and the relative magnitudes for the carboxyl carbons parallel in rough fashion the values for the corresponding ring carbons.

Both Bower et al.⁷ and Kasai and McLeod^{8,9} have discussed the structure of 2-pyridyl radical and Bower et al.⁷ have reported from studies on a frozen system observation of a 170-G ¹³C splitting which establishes this radical as of the σ type. The large value of the nitrogen splitting (~27 G) was observed in all studies but the proton hyperfine constants were not known before the present work because of the limited resolution available in the solid state studies.⁶⁻⁹ The INDO calculations in this case are not very helpful because they predict three proton splittings of comparable magnitude. Fortunately the pattern of splittings in Table III allows assignment to the various positions on the assumption that the position of the carboxyl group has little effect on the remaining splittings (as was observed for the phenyl radicals). The pattern of proton splittings is very different than that found with the phenyl radicals.

INDO calculations on 2-pyridyl radical were carried out for two geometries; calculated hyperfine constants are given in Table VI. The first (geometry A) used standard bond lengths²³ but ignored the difference between C-C and C-N bonds (i.e., a regular hexagon of bond length 1.40 Å) while the second (geometry B) used the geometry of pyridine following Kasai and McLeod.9 The results are quite similar except for smallest proton splitting, $a_3^{\rm H}$, which changes sign. The nitrogen splitting (17 G) is not in particularly good agreement with the observed 27 G. The results given by Kasai and McLeod⁹ which show a calculated 29-G value were obtained by using the INDO 2s spin density and the theoretical value of splitting for 100% 2s spin density. Although good agreement with observation is obtained, this procedure is questionable and use of the empirical parameter from the original INDO study should logically be preferred.

The origin of the very large nitrogen splitting for 2-pyridyl radical has been, in part, attributed⁷ to an in-plane π bond (involving the nitrogen lone-pair electrons) between the radical carbon and the nitrogen. We wish to point out that the spin densities given by the INDO calculation do not support such an effect. In particular one would expect large spin densities in the nitrogen in-plane p orbitals while the calculation for geometry A gives values of 0.011 and -0.003 for the orbitals along the 1-4 direction and at right

TABLE VI: Results of INDO Calculations on 2-Pyridyl Radical^{a-c}

	$a_2^{\mathbf{N}}$	a_3^{H}	a_4^{H}	a_5^{H}	a_6^{H}
Geometry A [°]	17,67	-0.61	6.73	8.49	7.26
Geometry B^d	18.66	0.35	5.64	9.51	7.70
Experimental	26.95	1.28	4.12	8.56	4.99
^a Positions numb	ered as				
	. 4				

^b Values in gauss. ^c Ring structure taken as a regular hexagon with all bond lengths 1.40 Å with CH bond length 1.08 Å. d Following Kasai and $McLeod^9$ this structure was taken as for pyridine (J. Rastrup-Anderson, J. Mol. Spectrosc., 2, 361 (1958)) with CH bond lengths 1.08 Å.

angles, respectively, while the 2s density is 0.047 (geometry B is similar). Thus a direct mixing of the nitrogen 2s orbital is mainly predicted. It should be pointed out in addition, however, that the small spin densities in the nitrogen p orbitals predicted by the INDO calculations probably cannot explain the relatively large anisotropy found for the ¹⁴N hyperfine interaction in both solid phase studies.^{6,7} Further study of this point is in order.

The one example of a 4-pyridyl radical (XX) has hyperfine constants similar to those of the phenyl radicals as might be expected and the assignment was made accordingly. The nitrogen splitting of 0.95 G can be compared with the para ¹³C splitting for phenyl radical VIII. It is usually found that ¹³C hyperfine constants are about twice those of ¹⁴N in a similar position.²⁷ Thus a value of around 2 is expected for the para carbon in a phenyl radical. The observed values are 1.3-1.8 G.

Summary

The present work provides, for the first time, solution spectra of phenyl and 2-pyridyl radicals and has allowed accurate measurement of the hyperfine constants. In the case of 2-pyridyl radical the proton splittings were not previously well known. It has also proved possible to determine the ¹³C hyperfine constants for four substituted phenyl radicals. The observation of a very large (~ 135 G) splitting by ¹³C at the radical site in these radicals has substantiated the σ nature of phenyl radical. The values of the g factors for both phenyl and 2-pyridyl radicals are below the free electron value as commonly observed for σ radicals. The other ring ¹³C hyperfine constants ($a_o \sim 7.5$, $a_m \sim 13$, $a_{\rm p} \sim 1.5$ G) are in approximate agreement with those predicted by INDO calculations. Hyperfine constants were also determined for ¹³C in the substituent carboxyl groups.

The observation of phenyl and 2-pyridyl radicals demonstrates in a direct way their formation in the two types of reaction used, namely, the decarboxylation of aromatic carboxylate ions by SO_4 . and the dissociative attachment of e_{aq}^{-} to aromatic bromides. The radicals with no ortho substituents are very reactive toward addition to another romatic ring and are best studied at starting material concentrations of <1 mM. Such low concentrations can readily be used with the bromides because of the high rate constant for reaction with e_{aq} ⁻. The unsubstituted phenyl radical, for example, was produced in this way from $5 \times 10^{-4} M$

bromobenzene. At higher concentrations of starting material (1-10 mM), such as used in the decarboxylation reactions, only the secondary adduct to another ring (a radical of the cyclohexadienyl type) is detected as with terephthalate or trimesate. This reaction, in part, explains the failure of Beckwith and Norman¹⁰ to directly observe phenyl radicals. When the radical has at least one ortho carboxyl group the secondary addition reaction is much slower and the phenyl radical is observed in the presence of 10 mM or more of aromatic. With compounds such as 1,2,3-benzenetricarboxylate there is a very marked preference for loss of the central CO_2^- upon reaction with SO_4 . A similar result is observed with 2,3-pyridinedicarboxylate in that loss at the 2 position is much more likely. In the case of 1,2,4-benzenetricarboxylate decarboxylation occurs at all three positions and direct observation of the two ortho-substituted phenyl radicals is possible while loss of the carboxyl group at the 4 position leads to a more reactive radical which adds to another molecule. The resulting adducts are observed.

NOTE ADDED IN PROOF: A. L. J. Beckwith, in a review paper [Intra-Sci. Chem. Rep., 4, 127 (1970)], has given hyperfine constants for two ortho-substituted phenyl radicals but gives no other details.

References and Notes

- Supported in part by the U.S. Atomic Energy Commission.
- V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben, Zh. Strukt. Khim., 3, (2) 709 (1962).
- J. E. Bennett, B. Mile, and A. Thomas, Chem. Commun., 265 (1965).
- P. H. Kasai, E. Hedaya, and E. B. Whipple, J. Am. Chem. Soc., 91, 4364 (1969);
 P. H. Kasai, P. A. Clark, and E. B. Whipple, *Ibid.*, 92, 2640 P (1970).
- S. Nagai, S. Ohnishi, and I. Nitta, J. Phys. Chem., 73, 2438 (1969). (5)
- J. E. Bennett and B. Mile, *J. Phys. Chem.*, **75**, 3432 (1971). H. J. Bower, J. A. McRae, and M. C. R. Symons, *Chem. Commun.*, 542

- (1) N. D. Dohar, J. A. Michae, and M. C. R. Symons, *Chem. Commun.*, 542 (1967); *J. Chem Soc. A*, 2696 (1968).
 (8) P. H. Kasai and D. McLeod, Jr., *J. Am. Chem. Soc.*, 92, 6085 (1970).
 (9) P. H. Kasai and D. McLeod, Jr., *J. Am. Chem. Soc.*, 94, 720 (1972).
 (10) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 403 (1969).
 (11) B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans.* 2 (1972) (1972). Trans. 2, 1272 (1972).
- (12) See, for example, G. E. Adams in "Advances in Radiation Chemistry", Vol. 3, M. Burton and J. L. Magee, Ed., Wiley-Interscience, New York, N.Y., 1972, p 125.
 R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc. B*, 1087
- (1970).
- K. Elben and R. W. Fessenden, J. Phys. Chem., 75, 1186 (1971).
 D. Behar and R. W. Fessenden, J. Phys. Chem., 75, 2752 (1971)
- (16)The 1,2,3,4- and 1,2,3,5-benzenetetracarboxylic acids were prepared by the permanganate oxidation of 1,2,3,4-tetramethylbenzene and 2,4,6-trimethylbenzoic acid, respectively. The resulting samples were recrystallized from water and showed elementary analyses in accord with their empirical formulae. Studies of the OH adducts to samples of these compounds (see ref 18) showed no evidence of other polycarbox-vic acids under a sensitivity sufficient to give the lines of the ¹³C conylic acids under a sensitivity sufficient to give the lines of the (17) G. Filby and K. G. Günther, J. Phys. Chem., 78, 1521 (1974).
 (18) K. Elben and R. H. Schuler, J. Phys. Chem., 78, 1521 (1974).
 (19) E. Hayon, A. Treinin, and J. Wolf, J. Am. Chem. Soc., 94, 47 (1972).
 (20) D. E. Pennington and A. Haim, J. Am. Chem. Soc., 90, 3700 (1968).
 (21) P. Neta and R. W. Fessenden, J. Phys. Chem., 78, 523 (1974).

- (22) Chemically induced dynamic electron polarization or abnormal ESR signal intensities has been shown to arise in systems of homogeneousl reacting radicals because the recombination rates of particular pairs of radicals depend upon the nuclear spin states. (R. W. Fessenden, J. Chem. Phys., 58, 2489 (1973).)
- (23)J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Am. Chem. Soc., 90, 4201 (1968).
- (24) D. J. Edge, R. O. C. Norman, and P. M. Storey, J. Chem. Soc. B. 1096 (1970)
- D. Behar and R. W. Fessenden, J. Phys. Chem., 76, 1710 (1972).
- (26)O. P. Chawla and R. W. Fessenden, to be submitted for publication; O.
- (26) O. P. Chawla and H. W. Pessenden, to be summary to publication, C. P. Chawla, Ph.D. Dissertation, Carnegie-Mellon University, 1973.
 (27) For Instance, the ¹⁴N splitting in NH₃⁺ is 19.5 G [T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961)] while that for ¹³C in CH₃ is 38 G [R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967)].