124.1 (s), 124.8 (s), 128.2 (d), 171.2 (s), 207.1 (s).

Methyl 4-(1-Cyclohexenyl)-3-(methoxycarbonyl)-2-methylbut-2-enoate (54). Method B/1 equiv KOAc yield: 36%. R_f: 0.6 (hexane/EtOAc 4:1, mixture of isomers *E* (83) and *Z* (17) as detected by ^{1}H NMR). IR (CCl$_4$) cm^{-1}: 1740, 1730, 1690, 1650, 1435, 1250, 1200, 1150, 1130, 1075, 1050. ^{1}H NMR (CDCl$_3$, major isomer *E*) δ: 1.4–1.6 (4 H, m, CH$_2$), 1.8–1.9 (4 H, m, CH$_2$), 1.99 (3 H, b s, Me), 3.11 (2 H, b s, CH$_2$), 3.71 (3 H, s, OMe), 3.74 (3 H, s, Me), 5.4 (1 H, b s, HC=). ^{1}H NMR (CDCl$_3$, minor isomer *Z*) δ: 1.4–1.6 (4 H, m, CH$_2$), 1.8–1.9 (4 H, m, CH$_2$), 1.98 (3 H, b s, Me), 2.91 (2 H, b s, CH$_2$), 3.70 (3 H, s, OMe), 3.73 (3 H, s, Me), 5.5 (1 H, b s, HC=). ^{13}C NMR (CDCl$_3$, major isomer *E*) δ: 17.7 (q), 22.2 (t), 22.9 (t), 25.3 (t), 28.1 (t), 39.2 (t), 51.7 (q), 51.9 (q), 123.6 (d), 132.5 (s), 134.2 (s), 137.3 (s), 169.1 (s), 169.3 (s). Anal. Calcd for C$_{14}$H$_{20}$O$_4$: C, 66.63; H, 8.01. Found: C, 66.98; H, 8.00.

Methyl 4-(1-Cyclohexenyl)-3-(hydroxymethyl)-2-methylbut-2-enoate (55). Method B/1 equiv KOAc yield: 91%. R_f: 0.51 (hexane/EtOAc 2:1; mixture of isomers *E* (89) and *Z* (11) as detected by ^{1}H NMR). IR (CCl$_4$) cm^{-1}: 3650, 3400, 1725, 1650, 1435, 1230, 1190, 1130. ^{1}H NMR (CDCl$_3$, major isomer *E*) δ: 1.48–1.66 (4 H, m, CH$_2$), 1.94 (3 H, b s, Me), 1.96–2.6 (4 H, m, CH$_2$), 3.11 (2 H, b s, CH$_2$), 3.70 (3 H, s, OMe), 4.2 (2 H, b s, CH$_2$O), 5.48 (1 H, m, HC=). ^{1}H NMR (CDCl$_3$, minor isomer *Z*) δ: 1.48–1.66 (4 H, m, CH$_2$), 1.75 (3 H, b s, Me), 1.96–2.6 (4 H, m, CH$_2$), 3.24 (2 H, b s, CH$_2$), 3.71 (3 H, s, Me), 4.0 (2 H, b s, CH$_2$O), 5.68 (1 H, b s, HC=). ^{13}C NMR (CDCl$_3$, major isomer *E*) δ: 15.4 (q), 22.4 (t), 22.9 (t), 25.4 (t), 28.4 (t), 40.0 (t), 51.6 (q), 62.2 (t), 123.3 (d), 127.0 (s), 136.2 (s), 143.5 (s), 170.2 (s). Anal. Calcd for C$_{13}$H$_{20}$O$_3$ (mixture of isomers *E* and *Z*): C, 69.60; H, 9.00. Found: C, 69.52; H, 9.00.

3-(Hydroxymethyl)-6-(methoxycarbonyl)-2-methylspiro[4.6]undec-2-en-1-one (40). Method A yield: 48%. Method B/1 equiv KOAc yield: 75%. R_f: 0.2 (hexane/EtOAc 2:1). IR (CCl$_4$) cm^{-1}: 3500, 3380, 1725, 1700, 1650, 1435, 1195, 1150, 1020, 910. ^{1}H NMR (CDCl$_3$) δ: 1.3–1.44 (4 H, m, CH$_2$), 1.64 (3 H, b s, Me), 1.71–1.78 (2 H, m, CH$_2$), 1.86–1.98 (4 H, m, CH$_2$), 2.55 (2 H, H$_a$, H$_{a'}$; q, *J* = 1.2 Hz, CH$_2$), 2.66 (1 H, H$_b$; d, *J* = 9.0 Hz, CHCO$_2$), 3.0–3.1 (1 H, m, OH), 3.55 (3 H, s, OMe), 4.51 (2 H, q, AB sys, δ$_A$ = 4.53, δ$_B$ = 4.49, J_q = 1.2 Hz, J_{AB} = 14.4 Hz, CH$_2$O). ^{13}C NMR (CDCl$_3$) δ: 8.1 (q), 23.7 (t), 26.7 (t), 30.4 (t), 30.6 (t), 38.8 (t), 44.2 (t), 50.5 (s), 51.6 (q), 53.5 (d), 60.4 (t), 134.2 (s), 166.2 (s), 174.9 (s), 212.9 (s). MS (FAB, Magic Bullet): 267 (M$^+$ + 1, 46), 235 (61), 207 (70), 189 (29), 175 (20), 161 (30), 133 (38), 119 (45), 109 (60), 105 (100). Anal. Calcd for C$_{15}$H$_{22}$O$_4$: C, 67.63; H, 8.34. Found: C, 67.56; H, 8.51.

3,6-Bis(methoxycarbonyl)-2-methylspiro[4.6]undec-2-en-1-one (41). Method B yield: 42%. Method B/1 equiv KOAc yield: 72%. R_f: 0.54 (hexane/EtOAc 4:1). IR (CCl$_4$) cm^{-1}: 1740, 1720, 1640, 1440, 1225.

Methyl 4-(1-Cyclohexenyl)-3-(methoxycarbonyl)-2-methylbut-2-enoate (54). [see above]

Methyl 4-(3-(Methoxycarbonyl)-2-methyl-1-oxospiro[4.6]undec-2-en-6-yl)-3-methyl-4-oxobut-2-enoate (56). Method B yield: 25%. R_f: 0.24 (hexane/EtOAc 4:1). IR (CCl$_4$) cm^{-1}: 1720, 1620, 1435, 1220. ^{1}H NMR (CDCl$_3$) δ: 1.1–1.9 (10 H, m, CH$_2$), 1.97 (3 H, d, *J* = 2.3 Hz, Me), 2.1 (3 H, b s, Me), 2.2–2.4 (1 H, m, CHCO$_2$), 2.5–2.8 (2 H, m, CH$_2$), 3.8 (3 H, s, OMe), 3.83 (3 H, s, OMe), 6.95 (1 H, q, *J* = 2.3 Hz, HC=). ^{13}C NMR (CDCl$_3$) δ: 10.3 (q), 16.0 (q), 23.3 (t), 25.8 (t), 30.4 (t), 30.5 (t), 39.7 (t), 43.7 (t), 49.2 (s), 51.9 (q), 52.2 (q), 58.9 (d), 135.6 (s), 145.4 (d), 147.4 (s), 147.9 (s), 166.1 (s), 166.8 (s), 197.8 (s), 213.6 (s). MS (FAB, Magic Bullet): 363 (M$^+$ + 1, 61), 345 (30), 337 (43), 263 (45), 235 (59), 167 (19), 91 (13).

3,6-Bis(methoxycarbonyl)-2-methylspiro[4.7]dodec-2-en-1-one (42). Method B yield: 47%. Method B/1 equiv KOAc yield: 63%. R_f: 0.3 (hexane/EtOAc 5:1). IR (CCl$_4$) cm^{-1}: 1740, 1715, 1650, 1435, 1370, 1220. ^{1}H NMR (CDCl$_3$) δ: 1.3–1.9 (12 H, m, 6 CH$_2$), 2.05 (3 H, t, *J* = 2.1 Hz, Me), 2.53 (2 H, H$_a$, H$_{a'}$; AB sys, q, δ$_A$ = 2.67, δ$_B$ = 2.40, J_q = 2.1, J_{AB} = 18.3 Hz, CH$_2$), 2.95 (1 H, H$_b$; dd, *J* = 2.7, 7.5 Hz, CHCO$_2$), 3.55 (3 H, s, OMe), 3.83 (3 H, s, OMe). ^{13}C NMR (CDCl$_3$) δ: 10.0 (q), 23.9 (t), 25.4 (t), 26.4 (t), 27.9 (t), 28.1 (t), 33.4 (t), 41.1 (t), 49.2 (d), 49.9 (s), 51.8 (q), 51.9 (q), 146.7 (s), 148.9 (s), 166.0 (s), 175.6 (s), 212.4 (s). MS (FAB, glycerol): 309 (M$^+$ + 1, 19), 277 (47), 249 (36), 217 (12), 167 (22), 115 (23), 105 (27). Anal. Calcd for C$_{17}$H$_{24}$O$_5$: C, 66.20; H, 7.86. Found: C, 65.90; H, 7.78.

Supplementary Material Available: Full X-ray data for structure determination of compounds 4, 18, and 34 (34 pages); tables of observed and calculated structure factors for 4, 18, and 34 (56 pages). Ordering information is given on any current masthead page.

ESR Study of the Photochemistry of Benzoic Acid Derivatives

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Abstract: Electron spin resonance (ESR) has been used to study radical intermediates in the photochemistry of a number of aromatic carboxylic acids, esters, anhydrides, amides, imides, and nitriles. Continuous photolysis was used to produce the radicals in either aqueous or alcoholic media. The triplet states of the compounds undergo two reactions in the presence of a hydrogen donor such as 2-propanol. A hydrogen atom is transferred to certain carbon atoms of the aromatic ring forming cyclohexadienyl radicals. In most cases, addition occurs at or opposite the carboxyl (or cyano) group. The pattern of addition is attributed to the higher spin density in the triplet at those positions. This pattern also correlates with the positions of higher hyperfine splitting in the corresponding anion radicals. In a parallel reaction, a hydrogen atom is also transferred to an oxygen of the carboxyl group (for acids, anhydrides, and esters) to form the one-electron-reduction product. The cyclohexadienyl radicals are not formed by protonation on a carbon of an anion radical. The ESR spectra of most of the cyclohexadienyl radicals are highly polarized to the extent that the low-field lines appear in emission. This effect is believed to be normal chemically induced dynamic spin polarization (CIDEP) as a result of cross reactions with the other radicals present.

Introduction

The present work began with an attempt to use continuous photolysis to produce the anion radical of terephthalic acid for study of its ^{13}C hyperfine constants (hfc's) in conjunction with

Qin et al.[1] Photolysis of acetone in the presence of 2-propanol was used to form (CH$_3$)$_2$ĊO$^-$ in basic aqueous solution, and that radical reduced the terephthalate. In addition to the desired anion radical, [$^-$O$_2$CC$_6$H$_4$CO$_2$$^-$]$^{•-}$, lines were observed from a cyclo-

(1) Qin, L.; Madden, K. P.; Schuler, R. H. *J. Phys. Chem.* 1988, *92*, 3790.

hexadienyl radical (CHD), resulting from net transfer of a hydrogen atom from the alcohol to a carbon bearing a carboxyl

group. Such a structure is different than that usually produced by direct addition of a radical to the ring, since addition is normally at an unsubstituted position. However, the ESR parameters of CHD radicals are so characteristic[2-5] that the identification of the structure of this radical is unambiguous. The present work describes the radicals observed with this and a variety of other related compounds and attempts to understand the reaction mechanism in more detail. It will be found that the radicals are the result of the reactions of the triplet states of the aromatic carboxylic acids. In cases of the appropriate symmetry—as with terephthalate—the triplet state reacts as a 1,4 biradical.

In addition to the interesting reaction pathway, the ESR spectrum observed with terephthalate showed a strong chemically induced dynamic electron polarization (CIDEP) in that the low-field lines of the CHD radical appeared in emission. Such a strong effect is unusual in steady-state photolysis spectra, particularly when the radicals involved are charged so that the radical–radical reaction rates are slowed by electrostatic repulsion. A separate publication will describe the results of time-resolved optical and ESR experiments using laser photolysis and will focus on the CIDEP effects. These time-resolved experiments confirm that a long-lived triplet state of terephthalate is formed (>80 μs in the absence of quenchers), that it can be sensitized by acetone triplet ($k = 1.3 \times 10^9$ M^{-1} s^{-1}), and that the triplet is quenched by 2-propanol. It is also clear that the CIDEP seen in steady-state ESR experiments (SSESR, continuous photolysis) is of the normal kind as a result of radical–radical reactions of the various radicals. The ionic strength of the high-pH solutions apparently is sufficient that radicals with several units of charge can react fast enough to produce CIDEP. The radicals are also found to have rather a long spin relaxation time (T_1) which increases the observed polarization.

The first ESR observations of the formation of CHD radicals from triplet states were by Sakaguchi et al.[6-9] They found CHD radicals from xanthone[6,8,9] and acetophenone and 2-acenaphthone.[7] The formation of CHD radicals was mainly with such hydrogen donors as triethylgermane, tributyltin hydride, and borohydride. Enhancement of the yield was found in polar solvents, and this effect was used to argue for the involvement of the $\pi\pi^*$ triplet as contrasted with the $n\pi^*$ state, which produced ketyl radicals.

Even though maleic anhydride and maleimide are not aromatic, the photolysis-ESR studies of these compounds by Roth et al.[10] and Ayscough et al.[11] may be relevant in a unified picture. Photolysis of maleic anhydride and maleimide in the presence of a hydrogen donor yields a cyclic alkyl radical produced by the addition of a hydrogen atom across the double bond and another radical by the addition of a solvent-derived radical also across the double bond. The ESR spectrum taken during continuous or steady-state photolysis (SSESR) of the cyclic alkyl radical showed the low-field lines in emission and high-field lines in absorption.

Photochemistry involving aromatic carboxylic acids, esters, anhydrides, amides, and imides has been studied in less detail than that of the family cousin, carbonyl compounds. Most of the neglect can be blamed on the low reactivity of the lowest triplet state which is of $\pi\pi^*$ character. Wagner et al.,[12] in a series of publications, emphasize the importance of the triplet $\pi\pi^*$ state for the formation of numerous interesting compounds. Arnold et al.[13] studied a series of aromatic esters, obtained the zero-field splitting parameters D and E, and used those parameters to show the nature of the lowest triplet state to be either "diallylic" or "quinoidal" (1,4 biradical) in nature. The phosphorescence spectrum has been used to identify the nature of the lowest triplet state for benzoic acid[14] and related compounds.[15] McLachlan[16] theoretically predicted the parallel between the spin distributions of the lowest excited triplet state and the corresponding anion radical. Hirota et al.[17] used ESR of the triplet states of cyano- and chloro-substituted benzene and pyridines to confirm McLachlan's prediction. In the case of benzonitrile, the triplet has a large hfc for the proton at the 4 position in accord with a quinoidal structure. Theoretical work done by Malar and Jug[18] on para-substituted benzenes and the recent work on p-xylene by Buma et al.[19] also predict the lowest triplet state to be of the "quinoidal" type.

Even though the triplet states of aromatic carboxylic acids and their derivatives have been studied by ESR, phosphorescence, and theoretical treatments, their reactions with different hydrogen donors have not been explored. The present work is an extensive study involving the photolysis of compounds of the above-mentioned types primarily by SSESR. A preliminary report was presented in 1988.[20] For most of the compounds studied, hydrogen atoms from hydrogen donors attach to the oxygen atom of the carbonyl chromophore, giving rise to a ketyl-type radical (at suitable pH, an anion radical), and also add to the ring, yielding a CHD radical. It will be found that the site of addition into the benzene ring is at the position of the maximum spin density of the corresponding triplet state.

Experimental Section

The continuous photolysis experiments were carried out with the light source and ESR spectrometer described by Davis and Fessenden.[21] The ESR spectrometer was a modified Varian V-4502 with a V-7000 9-in. magnet and a V-7200 power supply with a Fieldial MK II Hall Probe. The microwave frequency was measured with a Hewlett-Packard 5245L frequency counter with a 5255A converter, and corrections were made to line positions to compensate for changes in microwave frequency. The accuracy in the measurement of hyperfine constants varies with the size, with smaller values known to ±0.02 G and larger ones to about ±0.05 G. Measurements of relative g factors were made by comparison with the g factor of SO$_3$$^{·-}$ (2.00316[22]), and the second order effect[23] was also taken into consideration. A 100-kHz modulation frequency was used to give a first-derivative presentation.

The solution flowed at about 10 cm^3/min through a silica cell of 0.4-mm internal spacing in the ESR cavity. Photolysis was with light from a 1-kW Hg-Xe lamp in a housing with an elliptical mirror. A CoSO$_4$–NiSO$_4$ filter solution removed visible and IR wavelengths to reduce heating effects and allowed light from 250 to 300 nm to pass. The microwave cavity was kept at a constant temperature by circulating coolant from a constant temperature bath at 21 °C. For most of the experiments, the solution temperature in the cell ranged from 23 to 29 °C. Experiments with in situ radiolysis were done with the apparatus

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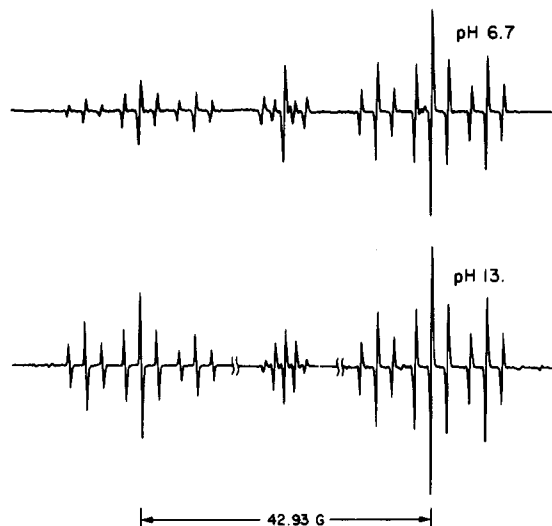
Figure 1. First-derivative ESR spectra taken during continuous photolysis of aqueous solutions of 10 mM sodium terephthalate and 10% 2-propanol at pH 6.7 (upper) and pH 13 (lower). Magnetic field increases to the right. The line group in the center is from the anion radical, and the two nine-line groups at high and low field are from CHD radical **6**. The amplification for the center portion of the lower trace was reduced by a factor of 40. The weak lines at the outer extremes in the lower trace are from radical **7**. Note that the first-derivative lines on the low-field side in the lower trace (pH 13) are opposite in phase to the other lines and so represent emission.

described earlier.[24] In this case the solution temperature was about 18 °C.

Unless otherwise mentioned, chemicals were obtained from Aldrich Chemical Company, Inc. The following chemicals were obtained from American Tokyo Kasei, Inc.: terephthalamide, *N*-methylphthalimide, and benzenepentacarboxylic acid. Trimellitic acid (benzene-1,2,4-tricarboxylic acid) was obtained from Ega-Chemie KG. 1,2,4,5-tetracyanobenzene was obtained from Pfaltz and Bauer Company. 1,3,5-tricyanobenzene was obtained from Fairfield Chemical Company. 1-Naphthoic acid, 2-naphthoic acid, and phthalic acid were obtained from Eastman Organic Chemicals. Naphthalene-1,6-dicarboxylic acid was purchased from Chemical Service Company. All the compounds were purchased in the purest form available, and most of them were used without any further purification. Acetone (Spectranalysed) and 2-propanol (Electronic grade) were obtained from Fisher Chemical Company.

Aqueous solutions were prepared in water from a Millipore Milli-Q water purifier. The pH was adjusted using potassium hydroxide and sulfuric acid. When 2-propanol was used as a hydrogen donor, the solutions were 10% by volume (1.3 M). For some experiments, 5% (v/v) of acetone (0.7 M) was used as a sensitizer. 2-Propanol was used as the solvent for all the other derivatives. Solutions were normally deoxygenated by bubbling with argon; N_2O was used when removal of e_{aq}^- was desired.

Results and Discussion

The ESR parameters of most of the anion radicals of aromatic carboxylic acids to be discussed were reported by Neta and Fessenden[25] from radiolysis-ESR experiments. The H and OH adducts to the aromatic acids were also studied in detail by Eiben and Schuler[4] using the same technique. More recently, the pK_a's of some of the hydroxycyclohexadienyl radicals were measured by Taniguchi and Schuler.[5] Neta and Fessenden[25] discussed the spin distribution in anion radicals of acids in terms of the symmetric (S, quinoidal) and antisymmetric (A, diallylic) orbitals
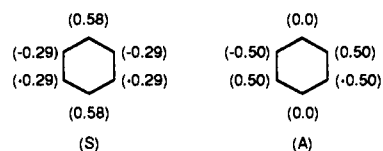
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Table I. ESR Parameters of Cyclohexadienyl Radicals Derived from Benzenecarboxylic Acids

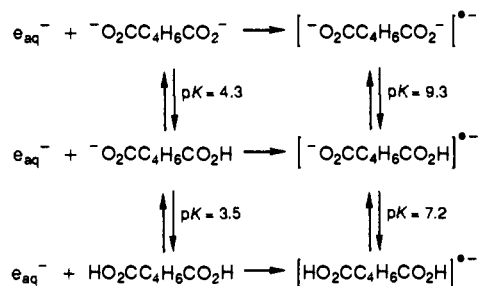| Compound	T[a]	I.D. No.	Radical	a_0^H	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	g factor
benzoate	S	1		44.51	8.06	2.35	--	2.35	8.06	2.00318
		2		44.98	8.94	2.69	13.02	2.69	8.94	2.00288
phthalate	A	3		44.9	7.65	—	—	2.58	8.52	2.0029
terephthalate	A	4		44.12	---	2.31	—	2.08	7.69	2.00326
		5		45.03	8.70	--	13.05	2.72	9.16	2.00285
isophthalate	S	6		42.93	8.16	2.39	—	2.39	8.16	2.00316
		7		45.96	--	2.82	12.25	—	7.63	2.00296
trimellitate	A	8		37.93	---	2.61	—	2.17	7.12	2.00326
		9		42.66	7.12	--	--	2.61	8.53	2.00306
	S	10		43.86	---	2.43	--	2.43	—	2.00330
		11		45.01	8.92	—	13.08	---	8.92	2.00280
	A	12		37.64	---	2.72	—	—	7.18	2.00320
	A	13		31.30	---	—	--	2.81	—	2.00332
	S	14		28.85	—	--	--	—	--	2.00317

[a] Symmetry of lowest $\pi\pi^*$ triplet state.

of benzene. In the following presentation, the spin distribution of the triplet states will also be discussed in terms of S and A orbitals. The numbers represent the Hückel molecular orbital coefficients.

Terephthalic Acid. Because the present work began with terephthalate and that system has been studied in most detail, it is advantageous to present those results first. In this way the reaction's mechanism will be made clear early in the presentation.

The first experiments began with the photolysis of a basic aqueous solution (pH 13) of terephthalate which also contained 5% (v/v) acetone and 10% 2-propanol. Similar ESR spectra are obtained from terephthalate with only 2-propanol present. The presence of acetone merely increased the radical concentrations somewhat. Spectra taken at pH 6.7 and 13 with only 2-propanol present are shown in Figure 1. Both spectra contain lines for the anion radical in the center and the two line groups of CHD radical **6** separated by the methylene proton splitting. The ESR parameters and structure are given in Table I. The parameters of the anion radical agreed with values determined by Neta and Fessenden.[25] Two aspects of the chemistry of this system are useful

for understanding the observations. The "anion" radical has pK_a values of 7 and 9,[26] so at pH 6.7, the anion radical is present as a monoanion while at pH 13 it is a trianion. In addition, the

$$e_{aq}^- + {}^-O_2CC_4H_6CO_2^- \longrightarrow \left| {}^-O_2CC_4H_6CO_2^- \right|^{\bullet -}$$

$$\updownarrow pK = 4.3 \qquad\qquad \updownarrow pK = 9.3$$

$$e_{aq}^- + {}^-O_2CC_4H_6CO_2H \longrightarrow \left| {}^-O_2CC_4H_6CO_2H \right|^{\bullet -}$$

$$\updownarrow pK = 3.5 \qquad\qquad \updownarrow pK = 7.2$$

$$e_{aq}^- + HO_2CC_4H_6CO_2H \longrightarrow \left| HO_2CC_4H_6CO_2H \right|^{\bullet -}$$

radical obtained from 2-propanol when a hydrogen atom is abstracted can reduce terephthalate.[26] This reaction is slower for the neutral form $(CH_3)_2\dot{C}OH$ (pK_a 12.0[27]) than for the dissociated form $(CH_3)_2\dot{C}O^-$. Some intensity of $(CH_3)_2\dot{C}OH$ is observed at near-neutral pH, so the lifetime of this radical with respect to the reduction reactions is comparable to that determined by radical–radical reactions (approximately 300 μs). The intensities of the lines of the anion radical, which are a good 1:4:6:4:1 quintet for pH 13, are perturbed at pH 6.7 because the radical is present as the monoanion and exchange of the carboxyl protons can occur. At pH 6.7, the concentrations of the anion and CHD radicals were comparable, while, at pH 13, the lines of the anion radical were much more intense by about a factor of 20 than those of the CHD radical. The ESR lines of the latter were also much more polarized to the extent that the low-field lines appear in emission (see Figure 1).

Also present at pH 13 were weaker lines of CHD radical **7**, some of which appear at the ends of the trace for pH 13 in Figure 1. The polarization complicates a comparison of the relative concentrations of the two radicals (**6** and **7**). However, a crude comparison is possible if the polarization factor is taken to be the same for the two CHD radicals. After taking account of the statistical weights of the lines measured, the relative concentrations of radicals **6** and **7** were found to be 9:1. The ^1H and ^{13}C hfc's of the anion radical (**1**) show the unpaired electron of the anion radical to be in an orbital of type S (quinoidal or 1,4 biradical), so the lowest $\pi\pi^*$ triplet should also have this spin distribution. The more prominent reaction to form CHD radicals at the 1 position (radical **6**) rather than at the 2 position (radical **7**) follows this pattern.
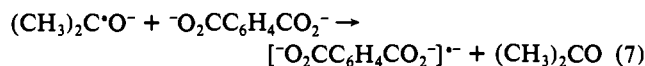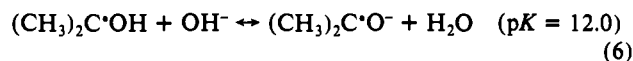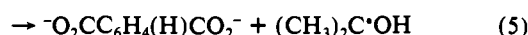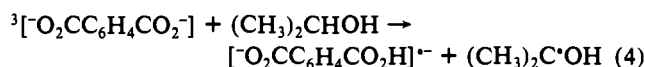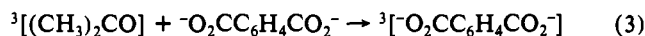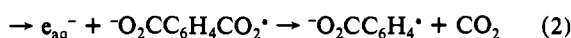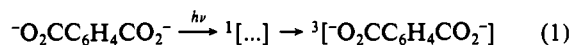
The system contains three radicals, namely, $(CH_3)_2\dot{C}O^-$, the anion radical, and the CHD radical from terephthalic acid. At pH 13, $(CH_3)_2\dot{C}O^-$ efficiently reduces[26] the terephthalic acid, increasing the concentration of the anion radical of terephthalate. Thus, the concentration of $(CH_3)_2\dot{C}O^-$ is small and should not contribute much to the polarization. The anion radical and CHD radical derived from terephthalic acid are multiply charged, so the rates of the reactions involving these radicals will be dependent on the ionic strength of the solution. Since the concentration of the anion radical is about 20 times greater than that of the CHD radical, the CHD radical can efficiently react with the anion radical. The SSESR results thus suggest that the CHD radical may be polarized by the cross reaction between the CHD radical and the anion radical.

In order to estimate the relaxation time for the terephthalate CHD radical, experiments using the ESR signal amplitude which is out-of-phase with the field modulation, as previously described,[22] were applied. The value of T_1 found for the CHD radical was 10 μs. This value is larger than that for many radicals such as $(CH_3)_2\dot{C}OH$, so a large polarization is not surprising.

When terephthalic acid was photolyzed alone at pH 13, the SSESR spectra contained lines from only the anion radical and a phenyl radical adduct to terephthalic acid. Photoionization of

the acid leads to decarboxylation and subsequent addition of the phenyl radical to the benzene ring of a parent molecule to form the adduct. The e_{aq}^- so produced reacts to form the anion radical. The ESR parameters of the phenyl adduct are the same as those of the phenyl adduct generated by $SO_4^{\bullet -}$ oxidation in a study by Zemel and Fessenden.[28] When 10% 2-propanol was added, the lines of the phenyl adduct disappeared and the spectra already described for pH 6.7 or pH 13 were seen. Phenyl radicals will abstract hydrogen from 2-propanol because of its much higher concentration than that of terephthalate.[29] Reaction of the e_{aq}^- ejected from terephthalate is not the only source of anion radical as shown by the comparable concentrations of that radical with or without acetone (which would scavenge all e_{aq}^-). Thus it is concluded that reaction of the triplet produces anion radical as well as CHD radicals.

The reaction mechanism which best describes these results is:

$$^-O_2CC_6H_4CO_2^- \xrightarrow{h\nu} {}^1[...] \rightarrow {}^3[^-O_2CC_6H_4CO_2^-] \quad (1)$$

$$\rightarrow e_{aq}^- + {}^-O_2CC_6H_4CO_2^{\bullet} \rightarrow {}^-O_2CC_6H_4^{\bullet} + CO_2 \quad (2)$$

$$^3[(CH_3)_2CO] + {}^-O_2CC_6H_4CO_2^- \rightarrow {}^3[^-O_2CC_6H_4CO_2^-] \quad (3)$$

$$^3[^-O_2CC_6H_4CO_2^-] + (CH_3)_2CHOH \rightarrow$$
$$[^-O_2CC_6H_4CO_2H]^{\bullet -} + (CH_3)_2C^{\bullet}OH \quad (4)$$

$$\rightarrow {}^-O_2CC_6H_4(H)CO_2^- + (CH_3)_2C^{\bullet}OH \quad (5)$$

$$(CH_3)_2C^{\bullet}OH + OH^- \leftrightarrow (CH_3)_2C^{\bullet}O^- + H_2O \quad (pK = 12.0) \quad (6)$$

$$(CH_3)_2C^{\bullet}O^- + {}^-O_2CC_6H_4CO_2^- \rightarrow$$
$$[^-O_2CC_6H_4CO_2^-]^{\bullet -} + (CH_3)_2CO \quad (7)$$

The extent of reaction 4 is hard to determine because of additional formation of the anion radical by reaction 7, but a certain amount of this reaction is supported by the data mentioned above.

Many features of this scheme are supported by optical laser photolysis experiments which will be published separately together with results from time-resolved ESR. The main conclusions from that work have been mentioned in the Introduction. The formation of the anion radical is readily seen by its strong optical absorption. It is not possible to detect the cyclohexadienyl radical optically as the absorption is expected to be weak ($\epsilon = 3000$ M^{-1} cm^{-1}) and in the same region as the very strong absorption at 360 nm of the anion radical ($\epsilon = 3 \times 10^4$ M^{-1} cm^{-1}). Thus the relative yield of the two radicals (anion and CHD) is not known.

Experiments were carried out with several other compounds as hydrogen donors including methanol, ethanol, glycerol, and tetrahydrofuran. With 10% by volume of methanol, glycerol, or tetrahydrofuran at pH 13, the ESR lines of the CHD radical were not as strong as with 2-propanol and the low-field group was only weakly in emission. The lines of the anion radical were comparable in intensity to those of the CHD radical. The spectrum with ethanol under similar conditions was somewhat stronger. When acetone was also present in this case, the anion radical lines were very strong, like those in Figure 1, but lines of $CH_3\dot{C}HO^-$ were also observed, showing that reduction of terephthalate by that radical was not very rapid but did occur.

When sodium borohydride was used as a hydrogen donor, the concentration of terephthalate anion radical was comparable to that of the CHD radical. In addition, the $\dot{B}H_3^-$ radical was observed. This spectrum is shown in Figure 2. The low-field lines of both the CHD radical and $\dot{B}H_3^-$ are in emission, and the high-field lines, in absorption. Both spectra change from emission to absorption near the same point in the spectrum (marked by the dashed line). The direct observation of polarization for $\dot{B}H_3^-$ and the comparable polarization that causes both spectra to change from emission to absorption at the same point in the spectrum suggest that the reaction of $\dot{B}H_3^-$ and the CHD radical causes the polarization. (The magnitude of the polarization also depends

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(27) Laroff, G. P.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 1283.

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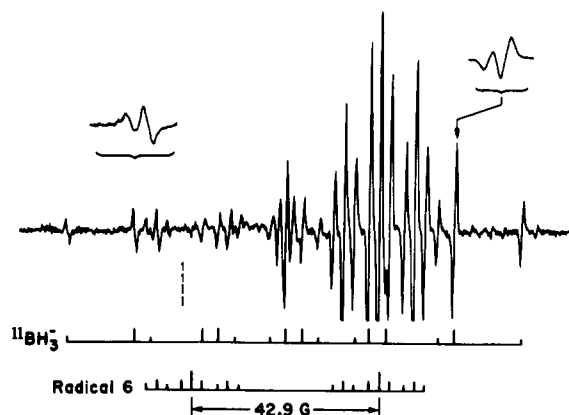
Figure 2. ESR spectrum taken during photolysis of a solution containing 10 mM terephthalate and 250 mM $NaBH_4$ at pH 13. The very strong asymmetry is the result of CIDEP, which makes the low-field lines either very weak or in emission. The two spectra indicated are from $^{11}\dot{B}H_3^-$ and CHD radical **6**. The dashed line indicates the point at which the lines change from emission to absorption. The inserts show the lines of overall intensity 3 (with second-order components of intensities 1:2) of $\dot{B}H_3^-$; the second-order splitting is 0.10 G. The low-field line was recorded at 4-fold higher amplification than the high-field line.

Table II. ESR Parameters of Anion Radicals Derived from Benzenecarboxylic Acids

Compound	T	I.D. No.	Radical	Hyperfine Constant (Gauss)						g factor
				a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	
	S	15		0.87^a	0.87^a	---	1.39	8.58	1.39	2.00347
	A	16		0.17^a	---	1.05	---	2.26	1.05	2.00347
		17		---	---	0.74	---	2.25	0.96	2.00349

^{a} Hydrogen-bonded protons.

on T_1.) The ESR parameters of the $\dot{B}H_3^-$ radical in water at 296 K are measured to be $a(^{11}B) = 19.25$ G, $a(3H) = 15.31$ G, and $g = 2.00190$, and the values are comparable to the isotropic values obtained from an irradiated solid sample.[30] Giles and Roberts[31] reported similar ESR parameters for $\dot{B}H_3^-$ radical in ether–alcohol solution at 253 K: $a(^{11}B) = 19.9$ G, $a(3H) = 15.3$ G, and $g = 2.0023$. It is interesting to note that the lines of this radical do not have excess width (see the inserts in Figure 2) as do those of $\dot{C}H_3$.[32]

Other Benzenecarboxylic Acids. Benzoate and many of the benzenepolycarboxylates were also photolyzed with 10% 2-propanol either with or without acetone. The CHD radicals observed are listed in Table I, and some anion radicals not reported previously are given in Table II. In all except the case of trimesate, ESR lines of the anion radical were seen. In that one case, no lines attributable to an anion are seen at high pH (but see below). The ESR spectra seen with benzenepenta- and benzenehexacarboxylates at pH 13 are shown in Figure 3. An intense line from the anion radical is seen in the center in each case, and lines from a CHD radical (4 and 2 lines, respectively) are seen in the outer portions of the spectra. The low-field lines appear in emission even for these very highly charged radicals. Broad lines at the ends of the recorded portion are from $(CH_3)_2\dot{C}O^-$. Further specific comments on the various aromatic
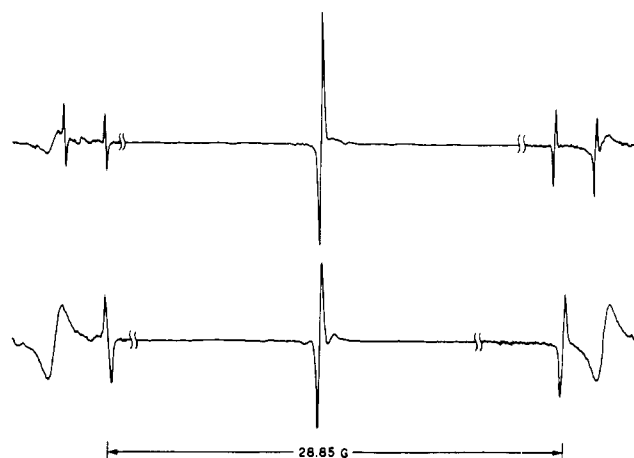
Figure 3. ESR spectra taken during continuous photolysis of aqueous solutions containing 5% acetone, 10% 2-propanol, and 3 mM benzene-pentacarboxylic acid (upper) and benzenehexacarboxylic acid (lower) both at pH 13. The center section was taken at an amplification 20-fold lower than the rest. The central line is from the anion radical, and the sharp outer lines (two pairs, upper; one pair, lower) are from CHD radicals **13** and **14**, respectively. The broad lines at the ends of the traces are from $(CH_3)_2\dot{C}O^-$.

acids can be made. Photolysis was at pH 13.

A. Benzoic Acid. When benzoate (20 mM) was photolyzed with 2-propanol, two CHD radicals, **1** and **2** in Table I, were detected. The low-field lines were in emission when acetone was present. No lines of the anion radical were detected.

B. Phthalic Acid. Only ESR lines of the anion radical were seen without 2-propanol. With 2-propanol, weak lines of the CHD radical **3** were also present. The low-field lines were not seen as a result of CIDEP, so the large hfc was determined by use of the g factor from the radiolysis experiment.[4] The hyperfine constants (hfc's) of 7.65 and 8.52 G were assigned to positions 1 and 5, respectively, on the basis of the value of 7.63 G for radical **7**, which is for a proton adjacent to a carboxyl group.

C. Isophthalic Acid. Photolysis with 2-propanol allowed lines of the two CHD radicals **4** and **5** to be detected. The low-field lines of both radicals were in emission. The hfc values for the 1 and 5 positions were assigned on the same basis as was used for radical **3**. The approximate concentration ratio for radicals **4** and **5**, measured as described above, is found to be 5:1.

D. Hemimellitic Acid. When hemimellitic acid (1,2,3-benzenetricarboxylic acid) was photolyzed in the presence of 10% 2-propanol and 5% acetone at pH 14, anion radical **15** in Table II was observed. There were two hydrogen-bonded protons present, so the pK_a for dissociation of those protons is greater than 14. No significant intensity of a CHD radical was found.

E. Trimellitic Acid. When trimellitic acid (1,2,4-benzene-tricarboxylic acid) was photolyzed at pH 13, two anion radicals (**16** and **17** in Table II) were formed. On the addition of 10% 2-propanol, CHD radicals **8** and **9** were obtained. The hfc values of 7.12 and 8.53 G in radical **9** are assigned to positions 1 and 5, respectively, in the same way as for radical **3**. The ratio of the steady-state concentrations of radicals **8** and **9** is 4:1. The ratio of the steady-state concentrations of the anion and CHD radicals is 4:1. When 5% acetone was added, this ratio became 20:1, indicating the efficient reduction of the acid by $(CH_3)_2\dot{C}O^-$.

F. Trimesic Acid. When trimesic acid (1,3,5-benzenetri-carboxylic acid) was photolyzed at pH 13, the ESR spectrum of a phenyl adduct to trimesic acid was observed.[28] This behavior is similar to that of terephthalic acid. Unlike the case of tere-phthalic acid, no ESR spectrum of an anion radical of trimesic acid could be observed. In the laser photolysis experiments with optical detection, the anion radical spectrum can clearly be seen and the existence of this species was confirmed by pulse-radiolysis experiments[33] also. In the ESR experiment, the anion radical could

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Table III. ESR Parameters of Cyclohexadienyl Radicals Derived from Pyridinedicarboxylic Acids

| Compound | T | I.D. No. | Radical | Hyperfine Constant (Gauss) | | | | | | g factor |
				$a_6{}^H$	$a_1{}^H$	$a_2{}^H$	$a_3{}^H$	$a_4{}^H$	$a_5{}^H$	
	A	18		43.66	---	3.15[a]	---	2.01	7.99	2.00307
	A	19		44.13	4.13[a]	2.61	---	1.52	---	2.00369
		20		42.09	9.14	3.51[a]	13.87	---	8.87	2.00269

[a] Nitrogen.

Table IV. ESR Parameters of Cyclohexadienyl Radicals Derived from Benzenecarboxylic Esters

| Compound | T | I.D. No. | Radical | Hyperfine Constant (Gauss) | | | | | | g factor |
				$a_6{}^H$	$a_1{}^H$	$a_2{}^H$	$a_3{}^H$	$a_4{}^H$	$a_6{}^H$	
	S	21		43.83	7.95	2.28	0.85[a]	2.28	7.95	2.00341
	S	22		47.54	9.17	2.79	13.25	2.79	9.17	2.00276
	A	23		40.13	0.54[a]	2.72	12.07	2.45	8.30	2.00298
	A	24		44.40	0.44[a]	2.63	0.75[a]	1.95	7.72	2.00325
	S	25		44.54	8.21	2.44	0.81[a]	2.44	8.21	2.00322
	S	26		45.00	0.41[a]	2.51	0.68[a]	2.51	0.41[a]	2.00352

[a] Methyl protons.

not be seen as a result of a Jahn–Teller effect which leads to a large ESR line broadening. Note however that the ESR spectrum of the singly protonated anion radical of trimesic acid was observed by Neta and Fessenden.[25] When 10% 2-propanol was added, radicals 10 and 11 in Table I were obtained. Radical 10 was observed in the radiolysis-ESR experiment also.[4] The concentration of radical 11 is only about 1% of the total CHD radicals formed.

When sodium borohydride was used as the hydrogen donor, the polarized spectra of $\dot{B}H_3{}^-$ and the CHD radical were seen. In addition to these radicals, the $\dot{B}H_3{}^-$ adduct to trimesic acid was also present. The ESR parameters of this adduct are $a(H)$ = 22.28 G, $a(^{11}B)$ = 25.22 G, $a(3H)$ = 0.26 G, $a(2H)$ = 1.59 G, and g = 2.003 50. Giles and Roberts[31b] have reported similar adducts of $\dot{B}H_3{}^-$ with a number of aromatics.

G. Pyromellitic Acid. When pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) was photolyzed, an anion radical spectrum was seen. On adding 10% 2-propanol, an increase in the concentration of the anion radical and the formation of the CHD radical 12 in Table I were observed.

H. Benzenepentacarboxylic Acid. When 10 mM benzenepentacarboxylic acid was photolyzed with 10% 2-propanol and 5% acetone, an intense signal of an anion radical and only one kind of CHD radical (13 in Table I) were found. The SSESR spectrum containing ESR lines of the anion radical and the CHD radical 13 and a partial spectrum of $(CH_3)_2\dot{C}O^-$ is shown in Figure 3. The concentration of the anion radical is about 20 times larger than that of the CHD radical.

I. Benzenehexacarboxylic Acid. When 3 mM benzenehexacarboxylic acid was photolyzed with 10% 2-propanol and 5% acetone, an intense signal of the anion radical and lines of CHD radical 14 in Table I were obtained. The SSESR spectrum containing ESR lines of the anion radical and the CHD radical 14 and several lines of $(CH_3)_2\dot{C}O^-$ is also shown in Figure 3.
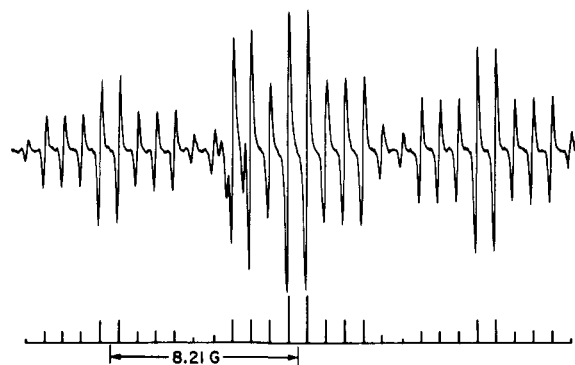
Pyridinecarboxylic Acids. Photochemical experiments were carried out with all the common pyridinemono- and pyridinedicarboxylic acids. All the acids invariably gave anion radicals,[34] but the CHD-type radicals were detected only with 2,6-pyridinedicarboxylic acid and 3,5-pyridinedicarboxylic acid. The former gave radical 18, and the latter gave radicals 19 and 20 in Table III. Both the radicals were as highly polarized as other CHD radicals obtained from benzenecarboxylic acids.

Benzenecarboxylic Esters. A. Methyl Benzoate. When 20 mM methyl benzoate was photolyzed in 2-propanol, radicals 21 and 22 in Table IV were seen. The concentrations of the two radicals were comparable. When 5% acetone was added, the low-field lines appeared in emission and the high-field lines in absorption. The radical pair involved in the CIDEP may be the CHD radical and $(CH_3)_2\dot{C}OH$ because the anion radical of the ester was not present. The splittings by the methyl protons in radical 21 were well resolved.

B. Dimethyl Phthalate. When 200 mM dimethyl phthalate was photolyzed in 2-propanol, CHD radical 23 in Table IV was obtained. The splittings by the methyl protons were well resolved.

Figure 4. The high-field line group of CHD radical 25 taken during photolysis of a solution of 10 mM dimethyl terephthalate in 2-propanol. Lines of $(CH_3)_2\dot{C}OH$ are present to the left of the center of this portion.

The lines of $(CH_3)_2\dot{C}OH$ were relatively prominent, and no significant intensity of an anion radical was found.

C. Dimethyl Isophthalate. On photolyzing 20 mM dimethyl isophthalate in 2-propanol, CHD radical 24 in Table IV was observed. The splittings by methyl protons of the ester groups were well resolved. Again, the lines of $(CH_3)_2\dot{C}OH$ were prominent and no anion radical was observed.

D. Dimethyl Terephthalate. When 10 mM dimethyl terephthalate was photolyzed in 2-propanol, CHD radical 25 in Table IV was obtained. The high-field lines of this radical are shown in Figure 4. Lines of $(CH_3)_2\dot{C}OH$ were present as well as a complex pattern near the center of the spectrum, which probably belongs to the anion radical. The latter spectrum was not analyzed.

E. Trimethyl Trimesate. When 15 mM trimethyl trimesate in 2-propanol was photolyzed, CHD radical 26 in Table IV was observed. The ESR spectra of all the CHD radicals obtained from the esters were strongly polarized, so that the low-field lines were observed in emission and the high-field lines in absorption under steady-state photolysis conditions.

Benzenecarboxylic Anhydrides. A. Phthalic Anhydride. When 20 mM phthalic anhydride in 2-propanol was photolyzed, an anion radical and CHD radical 27 in Table V were observed. The ESR parameters of the anion radical $\{a(H_{3,6})$ = 0.37 G and $a(H_{4,5})$ = 2.27 G; g = 2.00346$\}$ are similar to the values obtained by Sioda and Koski.[35] The steady-state concentration of the anion radical was about 5 times greater than that of the CHD radical.

B. Trimellitic Anhydride. On photolyzing 100 mM trimellitic anhydride (benzene-4-carboxy-1,2-carboxylic anhydride) in 2-

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Table V. ESR Parameters of Cyclohexadienyl Radicals Derived from Benzenecarboxylic Anhydrides

Compound	T	I.D. No.	Radical	a_6^H	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	g factor
	A	27		43.30	7.63	---	---	1.98	8.13	2.00305
	A	28		43.51	0.27[a]	2.61	---	---	7.29	2.00334
	A	29		38.33	0.27[a]	2.99	---	---	7.21	2.00325

(Hyperfine Constant (Gauss) spans columns a_6^H–a_5^H)

[a] Carboxyl proton.

Table VI. ESR Parameters of Cyclohexadienyl Radicals Derived from Benzenecarboxylic Imides

Compound	T	I.D. No.	Radical	a_6^H	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	g factor
	A	30		41.33	6.78	0.22[a]	0.82[b]	2.23	8.76	2.00325
	A	31		54.47	0.35[b]	4.11	11.75	2.39	7.64	2.00301
	A	32		40.54	6.42	0.33[a]	1.01[c]	2.23	8.92	2.00321

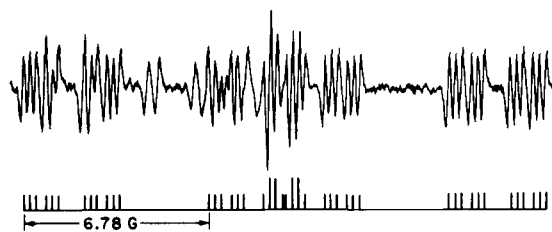(Hyperfine Constant (Gauss) spans columns a_6^H–a_5^H)

[a] Nitrogen. [b] NH proton. [c] Methyl proton.

Table VII. ESR Parameters of Anion Radicals Derived from Benzenecarboxylic Anhydrides and Imide

Compound	T	I.D. No.	Radical	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	g factor
	A	33		---	---	0.81	---	2.02	1.01	2.00345
	A	34		0.10[a]	---	0.47	---	---	0.47	2.00358
	A	35		2.80[b]	0.49[c]	0.49	2.06	2.06	0.49	2.00370

(Hyperfine Constant (Gauss) spans columns a_1^H–a_6^H)

[a] Carboxyl proton. [b] Nitrogen. [c] NH proton.

Figure 5. A high-field portion of the spectrum taken during photolysis of a 10 mM solution of phthalimide in 2-propanol. The line spectrum indicated is from CHD radical **30**. Lines of radical **31** and $(CH_3)_2\overset{\cdot}{C}OH$ are also present.

Table VIII. ESR Parameters of Cyclohexadienyl Radicals Derived from Benzamide and Cyanobenzenes

Compound	T	I.D. No.	Radical	a_6^H	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	g factor
	S	36		43.7	8.04	2.33	0.68[a]	2.33	8.04	2.0030
	S	37		43.1	7.97	2.31	1.99[a]	2.31	7.97	2.00306
	S	38		44.6	7.97	2.31	13.59	2.31	7.97	2.00296
	S	39		41.20	0.96[a]	2.61	1.62[a]	2.61	0.96[a]	2.00302

(Hyperfine Constant (Gauss) spans columns a_6^H–a_5^H)

[a] Nitrogen.

propanol, an anion radical and CHD radical **28** in Table V were observed. The ESR parameters of the anion radical **33** are given in Table VII. The concentration of the anion radical was about 10 times greater than that of the CHD radical.

C. Pyromellitic Dianhydride. On photolyzing 20 mM pyromellitic dianhydride (benzene-1,2,4,5-dicarboxylic anhydride) in 2-propanol, the anion radical **34** in Table VII and CHD radical **29** in Table V were obtained. The ESR parameters of the anion and CHD radicals indicate that one of the anhydride groups was hydrolyzed. The ESR parameters of the anion radical are similar to the values obtained from pyromellitic acid.[25] The CHD radical **29** was formed by the excited state abstracting hydrogen at one of the carbons attached to carboxyl groups which were formed by partial hydrolysis. The concentration of the anion radical was

about 5 times greater than that of the CHD radical. The SSESR spectra of the CHD radicals obtained from all the anhydrides were polarized like those of the acids and esters.

Benzenecarboxylic Imides. A. Phthalimide. When 100 mM phthalimide in 2-propanol was photolyzed, an anion radical **35** in Table VII and CHD radicals **30** and **31** in Table VI were obtained. The high-field group of lines of mainly radical **30** is shown in Figure 5. The ESR parameters of the anion radical are similar to the values reported by Sioda and Koski.[35] The concentration of the anion radical was about 5 times greater than that of the CHD radicals. The ratio of the concentration of CHD radicals **30** and **31** was 4:1. It is significant that the spectrum of the reduction product ("anion radical") is symmetric. This fact shows that the radical is, in fact, an anion, as the neutral species is not expected to show the symmetry.

The CHD radical **31** is a new type. The hfc of the methylene proton is 54.47 G and is greater than that of the methylene protons from the unsubstituted cyclohexadienyl radical.[3] The hfc of 48 G for the unsubstituted radical was explained by the way in which the spin density contributions from positions 1 and 5 combine.[4] The hfc of 54.47 G for radical **31** can be explained in an analogous way by taking into consideration the spin density at positions 1, 5, and 3' (−CO−). If it is assumed that the spin densities at 1 and 5 are equal, then the spin density at position 3' is estimated to be 0.025. The higher hfc may also be due to the intrinsic configuration of the radical, which leads to efficient overlap of the methylene hydrogen orbital with the p electron cloud.

B. *N*-Methylphthalimide. When 20 mM *N*-methylphthalimide in 2-propanol was photolyzed, an anion radical and the CHD radical **32** in Table VI were obtained. The ESR parameters of the CHD radical **32** are similar to those of CHD radical **30**. There was no radical found corresponding to a structure like that of radical **31**.

Benzamide and Cyanobenzenes. A. Benzamide. When 20 mM benzamide in 2-propanol was photolyzed, weak ESR signals from CHD radical **36** in Table VIII appeared. The low-field lines were not seen because of CIDEP. The methylene proton hfc was calculated using a g factor of 2.0030. When 20 mM terephthalamide in 2-propanol was photolyzed, the ESR spectrum of the anion radical alone was observed.
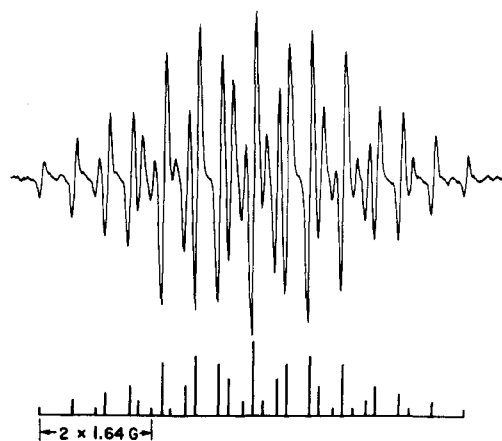
Figure 6. The high-field line group of CHD radical 39 taken during photolysis of a 10 mM solution of 1,3,5-tricyanobenzene and 5% acetone in 2-propanol. The splitting indicated is from ^{14}N at the 3 position.

Table IX. ESR Parameters of Cyclohexadienyl-Type Radicals Derived from Naphthalenecarboxylic Acids and Anhydride

Compound	I.D. No.	Radical	Hyperfine Constant (Gauss)								g factor
			a_{10}^H	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	a_7^H	
	40		28.93	7.83	---	<0.02[a]	3.59	1.80	---	1.03[a]	2.00322
	41		30.14	8.54	2.63	0.86	1.97	0.59	---	---	2.00332

[a] Carboxyl proton.

Table X. ESR Parameters of Anion Radicals from Naphthalenecarboxylic Acids

Compound	I.D. No.	Radical	Hyperfine Constant (Gauss)								g factor
			a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	a_7^H	a_8^H	
	42		---	1.25	1.25	---	2.14	0.88	0.88	2.14	2.00329
	43		---	4.76	0.59	6.66	1.62	---	3.73	0.59	2.00326
	44		2.75	---	3.12	0.69	2.75	---	3.12	0.69	2.00328
	45		---	1.55	1.55	---	---	1.55	1.55	---	2.00346

B. Benzonitrile. When 100 mM of benzonitrile was photolyzed in 2-propanol, two CHD radicals, 37 and 38 in Table VIII, were obtained. The splitting of nitrogen in the cyano group of CHD radical 37 can easily be resolved. The anion radical spectrum of the cyanobenzene was not seen.

C. 1,4-Dicyanobenzene. When 10 mM 1,4-dicyanobenzene was photolyzed in 2-propanol, only weak lines near the center of the spectrum were seen along with lines of $(CH_3)_2\dot{C}OH$. These new lines were not assigned.

D. 1,3,5-Tricyanobenzene. When 10 mM of 1,3,5-tricyanobenzene in 2-propanol was photolyzed, a strong ESR spectrum due to CHD radical 39 in Table VIII was seen. Figure 6 shows the high-field group of lines. Significant polarization was evident, but the low-field lines were still in absorption. (All the other CHD radicals in Table VIII showed a very strong CIDEP behavior where the low-field lines appeared in emission under steady-state photolysis conditions.) There was no evidence for the presence of the anion radical, but ESR line broadening due to the Jahn–Teller effect may make the lines unobservable as with the anion radical of trimesic acid.

Naphthalenecarboxylic Acids and Anhydride. Several naphthalenepolycarboxylates were photolyzed, and spectra were found which clearly belonged to analogues of CHD radicals. Spectra were found in several cases which showed only one large methylene proton hfc and have not been unambiguously assigned. These radicals may be OH or naphthyl radical adducts. Consequently, only those cases for which the structure is clear will be discussed. The parameters are given in Table IX. Parameters of the corresponding anion radicals are listed in Table X.

A. 1,4,5,8-Naphthalenetetracarboxylic Acid. When 2.5 mM of the acid alone at pH 13 was photolyzed, a spectrum was obtained containing intense lines of anion radical 45 in Table X, two sets of intense lines with 16 G spectral width which have not been assigned, and two kinds of CHD-type radicals. Of the CHD-type radicals, the set of lines with the largest total splitting—16 lines in each the high- and low-field groups—was more intense and showed the usual pattern of polarization with

the low-field side in emission. If these lines are assigned to a CHD-type radical with only one methylene proton, then the hfc has to be about 58 G. This value seems too large, so it is assumed that there are two equal splittings of value 28.93 G. The central lines cannot be seen because of the other intense lines in the center of the spectrum and the polarization which would make the intensity from the CHD radical very small. This radical is assigned as number 40 in Table IX. The hfc are very similar to those of the CHD radical from the next compound.

B. Naphthalene-1,8-carboxylic Anhydride. When 10 mM of the anhydride in 2-propanol was photolyzed, a moderately intense signal of an anion radical[36] and the CHD-type radical 41 in Table IX were obtained. The hfc of the methylene protons was 30.14 G. The other values were similar to those of radical 40. The assignment of hfc to the various positions was made by comparison with radicals formed by OH addition to some naphthalenesulfonic acids.[37] The results of that work show that the radical is basically a CHD radical only weakly affected by the presence of the second ring. The expected hfc's at the 1, 2, and 3 positions are about 9, 2.6, and 13 G, just as in cyclohexadienyl radical itself.[2]

Steady-State Radiolysis Experiments. In a discussion of the substitution reactions of cyanobenzenes[38,39] and some phthalimides,[40] it was suggested that the precursor for the CHD radical is an anion radical. The anion radical would protonate on a carbon, and the CHD radical thus formed would then be responsible for the substitution reaction. In the present investigation, there are systems where both the anion radical and CHD radical are formed. Several experiments were carried out to test the conversion of anion to CHD radical. A steady-state radiolysis experiment was done with an aqueous solution containing 1.25 M 2-propanol to convert H and OH produced by the radiolysis into $(CH_3)_2\dot{C}O^-$. This radical (and e_{aq}^- from the radiolysis), in turn, reduced the terephthalate and produced a large concentration of the anion radical. Under these conditions, there were no ESR lines of the CHD radical. An alternative photolysis experiment was carried out using the anion of p-cresol to produce e_{aq}^- in the presence of terephthalate. Again, a large concentration of the anion radical of terephthalate was produced and no ESR lines from the CHD radical were seen. In this aqueous system the anion radical does not, therefore, convert into a detectable amount of CHD radical. Such a conversion is unlikely in solvents such as 2-propanol as well.

A radiolysis experiment can also be used to confirm the nature of the radicals involved in the polarization mechanism. A flowing-nitrogen-purged terephthalic acid solution at pH 12 was irradiated by a 2.8-MeV electron beam. Radiolysis of water yields comparable amounts of e_{aq}^- and hydroxyl radical. The e_{aq}^- adds to the terephthalate to form the anion radical while the hydroxyl

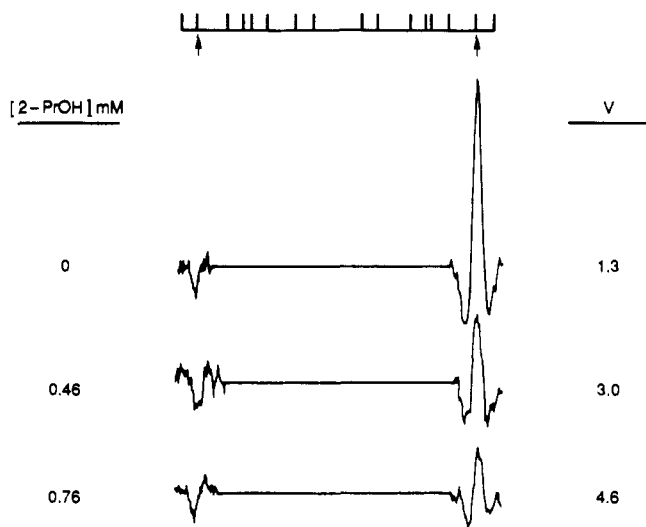(36) The hfc are 6.02, 5.50, and 1.14 G each for pairs of protons and g = 2.00297.

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Figure 7. Symmetrically located lines in the spectrum of the hydroxy-cyclohexadienyl radical formed by addition of OH to the 2 position of terephthalate (10 mM) at pH 13. The concentration of 2-propanol and the enhancement factor, V, are indicated.

radical adds to the ring to form the hydroxycyclohexadienyl radical. With these comparable production rates of the two radicals, the low-field lines of the ESR spectrum of the hydroxycyclohexadienyl radical were observed in emission and the high-field lines in absorption. Thus the various bimolecular radical reactions are rapid enough to produce substantial polarization even though the absolute signal size (radical concentration) is not particularly large.

The relative concentration of the anion radical can be increased by the addition of a small concentration of 2-propanol. The reaction of OH with the alcohol will compete with addition to terephthalate, thus decreasing the formation of the hydroxy-cyclohexadienyl radical and forming more anion radical (via reaction 7). Under the conditions described above, the solution contains only the two radicals (plus a small concentration of the H atom adduct). The ratio of the two concentrations depends on the concentration of 2-propanol, but the total concentration is constant. In Figure 7, corresponding lines in the low-field and high-field groups are shown at different concentrations of the anion radical. The enhancement factors (V) for the high-field line in Figure 7 at different concentrations of the anion radical are also given. The enhancement factor[41] is the ratio of the anomalous population value to the Boltzmann value and is calculated from the (algebraic) difference of the amplitudes of the low- and high-field lines divided by the sum. The increase in the enhancement factor is an indication of the increase in the polarization. Since the polarization of the CHD radical is increased by increasing the concentration of the anion radical, it is evident that the polarization is the result of the cross reaction between the CHD radical and the anion radical. This result supports the proposal of the involvement of the cross reaction in the polarization mechanism with the photolytic system where the only difference is the detailed structure of the CHD.

Photochemical Reaction Mechanism. It is interesting to note that, in the photochemical hydrogen abstraction reactions, the hydrogen atom is transferred to the benzene ring at different positions than observed in the direct H atom addition in radiolysis experiments. Thus, CHD radicals of different structure are found in the two kinds of experiments. In direct addition of a hydrogen atom, the site of reaction is predominantly the unsubstituted positions with only a weak directing effect corresponding to the electrophilic nature of the hydrogen atom as shown by Neta and Schuler.[42] The pattern of reactivity observed here apparently follows the spin density distribution in the triplet state, which in

turn is similar to that in the anion radical as mentioned in the Introduction. The spin distribution in anion radicals, in turn, has been discussed in terms of the symmetric (S) and antisymmetric (A) orbitals in benzene given above. Since carboxyl is an electron-withdrawing group, it will stabilize the orbital with the largest spin density at the site of substitution. The anion radicals of benzoate and terephthalate should then have large spin densities at the 1 and 4 positions. The hfc for the anion radical of benzoate[25] with the largest value at the 4 position clearly follows this quinoidal pattern, so the orbital is of the S type. Thus radicals 1 and 2 are formed by H atom transfer to the 1 id 4 positions of the benzoate triplet. With terephthalate, the pattern is similar and radical 6 is the major product with a minor reaction to form radical 7. Phthalate is a more complex case. Here the orbital of the anion radical is of the A type with the carboxyl groups both on the same side of the nodal plane. The observed CHD radical is formed by transfer to the positions of high spin density (or orbital coefficient) opposite one of the carboxyl groups. This rule essentially means that reaction is at or opposite a carboxyl group, and this rule works for all the benzene derivatives shown in Table I, with minor products in certain instances (terephthalate). In the case of trimellitate, the observed sites of addition are controlled by two carboxylate groups, as is true for benzenepentacarboxylate. The esters in Table IV are similar. The CHD radicals from the two pyridine derivatives also follow this pattern.

The CHD radicals from the anhydrides, in each case, follow the rule that the reactive position is opposite a carboxyl group. With pyromellitic dianhydride in 2-propanol, the radical seems to come from a partially hydrolyzed source. The two phthalic imides reacted as did the anhydride, with the exception that a second species was found with phthalimide. This CHD radical (31) is unique in that it is bridged at the methylene position. A possible reason for the larger methylene proton hfc has been discussed above. No special comment is required on benzamide. The nitriles behave much as the corresponding carboxylates with reaction at the 1 or 4 positions.

The steady-state ESR results using photolysis and radiolysis and the TRESR and flash photolysis experiments all are in agreement in most ways with the reaction mechanism, reactions 1–7, given above. The main question involves the relative ratios of competing reactions 4 and 5 and how they vary with the hydrogen donor. When BH_4^- is the donor, very little of the anion radical is formed. This result is like that observed by Sakaguchi et al.[6] who also found the cyclohexadienyl-type product to be favored by hydride donors. Because of reaction 7, it is hard to determine how much the direct transfer of a hydrogen to the oxygen of the carboxyl group, reaction 4, contributes to the yield of the anion radical. Time-resolved ESR experiments with 308-nm excitation give an opportunity to answer this question, but a detailed discussion is beyond the scope of this paper. However, the results found so far[43] seem to show that at least some anion radical is formed directly. The rate constant for reaction 7 given by Qin et al.[26] predicts that this reaction has a period of 6 μs at 10 mM terephthalate, so in basic solution the anion radical is formed rapidly relative to its subsequent lifetime. The corresponding reaction with the form $(CH_3)_2\dot{C}OH$ is expected to be much slower, so the formation of anion radicals in neutral solution may indicate transfer of hydrogen to the triplet, reaction 4. Under those conditions (see Figure 1), the anion is present to a lesser extent than in basic solution and lines of $(CH_3)_2\dot{C}OH$ are observed. The formation of reduced forms of phthalimide and 1,8-naphthalic anhydride in 2-propanol solution can be shown to be clearly the result of transfer of hydrogen rather than subsequent reduction. If acetone is added to the solution, the concentration of $(CH_3)_2\dot{C}OH$ is much increased but the anion radical is only present at a small concentration. Thus, $(CH_3)_2\dot{C}OH$ is a poor reductant for these compounds in 2-propanol medium. It is interesting that the reduced forms of the imide and anhydride are

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(43) The time-resolved experiments show that lines of the anion radical are present within a few μs of the laser pulse in neutral solution. The radical $(CH_3)_2\dot{C}OH$ is also present but disappears only slowly.

present as anions in 2-propanol. The ESR spectra clearly show a symmetry which would not be present if one carbonyl group were protonated. These reduced forms are much more acidic than the corresponding ketyl radicals formed from simple ketones (for example benzophenone) and so can dissociate to the monoanion in 2-propanol. The papers of Sakaguchi et al.[6-9] suggest that $n\pi^*$ triplet states react at the oxygen of the carbonyl (carboxyl here) and that $\pi\pi^*$ states react on the ring. In the picture given here, it is suggested that a given triplet state, such as that of terephthalate, has electron density on both oxygen and ring carbon atoms and can accept hydrogen at both sites.

Mazzochi et al.[40] have exhaustively studied the photochemistry of phthalimides and N-substituted phthalimides and photochemically synthesized a large number of interesting compounds, where the activity is mainly in the five-membered ring. Two recent attempts reporting cycloaddition reactions[44,45] involving the benzene ring of phthalimide are interesting and open a whole new area of exploration. Our results which demonstrate the nature of the lowest $\pi\pi^*$ triplet state of phthalimide to be of type A may be able to explain the involvement of the $\pi\pi^*$ triplet state in the formation of the cycloaddition products. In this context, we hope that the detailed study presented here may be useful to organic photochemists and may lead to synthesis of new compounds.

Product studies have been done for the photochemical reaction between benzonitrile and an alkylbenzene.[38,39] Products were observed where the cyano group was replaced by either the benzyl radical or by a hydrogen atom. It was proposed that the anion radical is protonated to give a CHD radical, which upon further reaction gives the desired product. The present work shows that, in the cases examined, the anion radicals do not produce CHD radicals. However, transfer of hydrogen to the triplet states often does form these radicals.

The source of the CIDEP probably involves different reactions under different conditions. With terephthalate in strongly basic solution, $(CH_3)_2\dot{C}O^-$ rapidly reduces the acid,[26] so the polarization must come from either reaction of the CHD radical with itself or cross reaction with the anion radical. At first sight, the reaction of doubly charged radicals should not be rapid, but the high ionic strength makes such a reaction sufficiently rapid, as shown by time-resolved experiments. This effect is most striking for such species as the CHD radicals from the higher polycarboxylates. In neutral solution, as in Figure 1, $(CH_3)_2\dot{C}OH$ remains for a longer time before reacting and may also participate by reacting with the CHD radical. The observed polarization under these conditions is smaller. With the penta- and hexacarboxylates in the presence of 2-propanol, as in Figure 3, $(CH_3)_2\dot{C}O^-$ is still present, as shown by its broad lines, and so may also cross react with the CHD radical. In the experiment with BH_4^- (Figure 2), the only significant concentrations are of the CHD radical and $\dot{B}H_3^-$. It is possible that the self reactions of each radical with

another of the same structure account for the polarization. However, cross reactions of the two species are probably also involved. The effectiveness of the cross reaction is also enhanced by the formation of anion radical (by reaction 7), which is less reactive by self reaction. In a steady-state experiment, there will be an accumulation of the anion radical so any new CHD radical can react with it. The effectiveness of cross reactions when one of the radicals is persistent has been described by Fischer.[46]

Summary

Aromatic compounds with structure Ph–CO–X (X = OH, OR, NH_2, –NH–, –O–) are excited by UV light (250–300 nm) to an upper singlet state and by intersystem crossing go to a triplet state. The precursor for the following photochemistry is apparently the lowest $\pi\pi^*$ triplet state. In the presence of a hydrogen donor like 2-propanol, addition of the hydrogen atom at the oxygen atom of the carbonyl group produces a carbonyl reduced species and the addition of the hydrogen atom to the benzene ring gives rise to a CHD radical. At suitable pH, deprotonation of the carbonyl reduced species yields the anion radical. The position of the addition of the hydrogen atom to the benzene ring depends on the spin distribution of the $\pi\pi^*$ triplet state and the orbital type can be either S or A. In either case, the hydrogen is transferred to a site at or opposite the carboxyl or related group. The concentration of the anion radical is also increased by the efficient reduction of the parent acid by $(CH_3)_2\dot{C}O^-$ at pH > 12. Invariably, the SSESR spectrum of the CHD radical is highly polarized, where all the low-field lines are in emission and the high-field lines in absorption.

When the study is extended to substituted cyanobenzenes, the behavior for cyano- and 1,3,5-tricyanobenzene is similar to that of the above compounds. The study was also extended to naphthalene compounds, and the results are similar to those of the benzene compounds for at least some of the systems. Various observations including time-resolved ESR results (not discussed in detail) indicate that the radical pair mechanism is responsible for the observed CIDEP. The radical pair involved is usually the CHD radical and the anion radical, but in some cases $(CH_3)_2\dot{C}OH$ or $(CH_3)_2\dot{C}O^-$ may also be involved.

When sodium borohydride was used as a hydrogen donor to quench the triplet state of trimesic acid, a cyclohexadienyl $\dot{B}H_3^-$ adduct was present along with the cyclohexadienyl hydrogen atom adduct. Methyl radical and $\dot{B}H_3^-$ are isoelectronic but the corresponding methyl adduct is not known so far. The formation of the $\dot{B}H_3^-$ adduct indicates an increased reactivity of the $\dot{B}H_3^-$ radical.

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