

- to a weighted average of singlet and triplet states of the diradical,¹⁷ and in cases such as the 1,4-cyclohexadiyl diradical where the two electrons can interact, the singlet-triplet splitting can be large and the singlet diradical energy will be seriously underestimated. It would be amusing if the calculation which prompted the recent search for the diradical mechanism were to be in error.
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Absolute Rate Constants for Reactions of Phenyl Radicals¹

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Abstract: The absolute rate constant for the addition of *p*-carboxyphenyl radical to *p*-bromobenzoate anion in aqueous solution has been determined by optical pulse radiolysis and time-resolved ESR experiments to be $7.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (corrected to zero ionic strength). The rate constants for addition of phenyl radicals to typical aromatic systems should be of this same magnitude. Addition of *p*-carboxyphenyl radical to benzene occurs with a similar rate constant and results in the formation of a substituted cyclohexadienyl radical that can be quantitatively oxidized to biphenyl-4-carboxylic acid. Abstraction from hydrogen donors results in the quantitative formation of benzoic acid. By reference to the absolute rate for addition to *p*-bromobenzoate the rate constant for H abstraction from isopropyl alcohol has been determined from competitive measurements of benzoic acid formation to be $5.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Measurements by optical pulse radiolysis and time-resolved ESR methods give comparable values. H atom abstraction from other alcohols is found to be only modestly slower. It is clear from these measurements that the lifetime of phenyl radicals in the presence of most organic materials will usually be very low so that reactions second order in phenyl radicals will not normally be important.

Introduction

In spite of the considerable importance of the reactions of phenyl radicals in organic chemistry,² there have been only a few sporadic attempts to determine the absolute rate constants for these reactions. Cercek and Kongshaug,³ in pulse radiolysis studies on aqueous solutions of iodobenzene and *p*-bromophenol, attributed increases in the optical absorption at 270 nm to the addition of phenyl and *p*-hydroxyphenyl radicals to the starting materials. In the latter case they estimated a rate constant of $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Bhatia and Schuler⁴ used this value as a reference and from relative rate measurements determined a rate constant of $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for abstraction of hydrogen from isopropyl alcohol by the *p*-hydroxyphenyl radical. Packer et al.⁵ found that the radiolysis of toluenediazonium cation in aqueous solutions containing methanol induced a chain reaction with the methanol and from an assumed chain length estimated a rate constant $>10^5$ for

abstraction of H from the methanol by the *p*-methylphenyl radical. Janzen and co-workers using spin trapping methods have estimated the rate constant for addition of phenyl to benzene to be $10^5 \text{ M}^{-1} \text{ s}^{-1}$ and have determined the relative rates for abstraction of hydrogen from the simple alcohols.⁶ Very recently Lorand and coworkers⁷ have compared the reactions of phenyl radicals with diffusion limited reactions and have estimated $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant for H abstraction from secondary alcohols and $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for addition to benzene. Although it is clear that the rate constants for the reactions of phenyl radicals are considerably greater than those for similar reactions of π radicals, there is at the present time a considerable uncertainty in the literature as to the exact magnitude of the rate constants. Knowledge of the absolute values of these rate constants is important so that one can properly take into account various competing processes and define the limiting phenyl radical concentration attainable in a given experimental situation.

Currently available optical and ESR spectroscopic pulsed methods make possible detailed measurements on the absolute rate constants for the reaction of phenyl radicals. The optical measurements are somewhat complicated by the fact that phenyl radicals absorb very weakly and in a region (i.e., below 300 nm) which is masked by other absorbing species. We have chosen to follow the reaction indirectly by examining the increase in absorption ascribable to the substituted cyclohexadienyl radicals produced by the addition of the phenyl radicals to aromatic systems. Since these latter species absorb only modestly (i.e., with maximum extinction coefficients of $\sim 3000 \text{ M}^{-1} \text{ cm}^{-1}$) and must be examined at concentrations of only $\sim 10^{-6} \text{ M}$, signal averaging methods such as those developed during recent years⁸ can be used to great advantage. In the ESR studies the disappearance of the phenyl radicals, where the spectral parameters are known from steady-state experiments,⁹ can be followed directly. The reaction assignments used in the kinetic scheme are supported by liquid chromatographic analyses of the radiation produced products which demonstrate rather conclusively that these assignments describe the quantitative aspects correctly. For experimental reasons the present study has been carried out on *p*-carboxyphenyl radicals produced by the radiolytic reduction of *p*-bromobenzoate anions. The presence of the *p*-carboxy substituent should not affect the reaction kinetics seriously and the results of the measurements made here should be reasonably representative of the reactions of most simple phenyl radicals.

Experimental Section

Product Studies. Products from the radiolysis of aqueous solutions 10^{-3} M in *p*-bromobenzoic acid were examined by liquid chromatographic methods.^{4,10} In the present study a Perkin-Elmer LC55 spectrophotometer having a noise level $\sim 10^{-4}$ absorbance units was used as the chromatographic detector. Benzoic acid produced by H abstraction reactions of the *p*-carboxyphenyl radicals was determined directly on 0.2 cm^3 of the irradiated solution. Separation was on a 1-m column of either Du Pont Permaphase AAX or Zipax SAX using as the eluent 0.02 M acetate buffer at pH 4.65 containing 2–4 mM sodium perchlorate. Detection was at 230 nm. Reaction of the *p*-carboxyphenyl radical with benzene was monitored by oxidizing the resultant cyclohexadienyl radicals with ferricyanide and determining the biphenyl-4-carboxylic acid produced chromatographically. This latter product was concentrated 2.5-fold by extracting 25 mL of the irradiated solution three times with CHCl_3 after acidification to pH 1.5. The resultant CHCl_3 solution was separated on a $0.25\text{-m } \mu\text{-Porasil}$ column (Waters Associates) using a 5:1 isooctane-dioxane mixture containing 0.2% acetic acid. In this case detection was at 268 nm. The chromatographic sensitivities were determined using appropriate reference samples of benzoic acid (Baker Analyzed Reagent) and biphenyl-4-carboxylic acid (Aldrich Chemical Co.).

Solutions for these irradiations were prepared from quadruply distilled water, buffered to pH 7.0 ± 0.2 with 1 mM phosphate buffer and purged of oxygen by bubbling in the irradiation cell with nitrogen. In the study of addition to benzene the experiments were carried out on saturated solutions (20 mM in benzene) by adding 0.1 cm^3 of degassed benzene to 25-cm^3 samples after purging the latter. Most irradiations were in a cobalt-60 source for 2 min at an absorbed dose rate of $4.7 \times 10^{17} \text{ eV g}^{-1} \text{ min}^{-1}$. The studies with benzene and ferricyanide were carried out at a dose rate of $3 \times 10^{16} \text{ eV g}^{-1} \text{ min}^{-1}$.

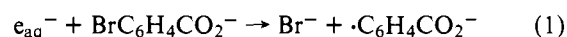
Optical Pulse Radiolysis Studies. Optical spectra of the reaction intermediates were taken on the microsecond time scale using the computer-controlled pulse radiolysis apparatus described by Patterson and Lilie⁸ with the software modification previously described.¹¹ As described below, the cyclohexadienyl radicals produced by addition of phenyl radicals to bromobenzoate absorb more toward the red than do the related radicals produced by H and OH addition so that their formation kinetics can be followed unambiguously. Solutions of the bromobenzoate were purged of oxygen by bubbling with nitrogen and a flow system was used to replenish the sample between pulses. The bromobenzoic acid was neutralized with NaOH and then buffered to pH 7 with millimolar phosphate buffer. Doses were such that initial phenyl radical concentrations were $\sim 2 \times 10^{-6} \text{ M}$ at which concen-

tration the product carboxyphenylcyclohexadienyl radicals did not decay appreciably over the $\sim 75 \mu\text{s}$ used in most observations. Because the signals were low ($< 10^{-2}$ absorbance units) signal averaging methods were used to improve the quality of the traces; e.g., the data from 25–50 experiments were averaged in most kinetic studies. The absorbance measurements given here are compared to $(\text{SCN})_2^-$ with a reference value of $7600 \text{ M}^{-1} \text{ cm}^{-1}$ taken for the extinction coefficient at 480 nm and a yield of 6.0 in N_2O saturated solution. Spectral data were processed as previously described.¹² Kinetic analysis was carried out by fitting a least-mean-square exponential growth to the observed data. Since the carboxyphenyl radical is charged, effects of ionic strength on its reaction kinetics must be properly taken into account. Unless otherwise stated, rate constants reported here are corrected to zero ionic strength.

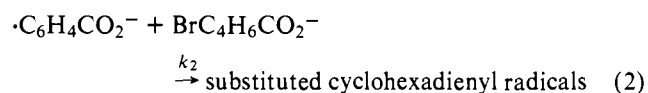
Pulse Radiolysis-ESR Spectroscopy. The time-resolved ESR spectroscopic methods described by Verma and Fessenden^{13,14} were used to examine directly the loss of carboxyphenyl radicals from pulse radiolyzed solutions in a flow system. Studies were carried out both on aqueous solutions of bromobenzoate alone and also on solutions to which isopropyl alcohol had been added. In this case KOH was used to make the solutions basic and measurements were carried out at a pH of ~ 11.5 . Doses in these experiments were an order of magnitude higher than in the optical studies and appreciable second-order decay took place on the $10\text{-}\mu\text{s}$ time scale (50% decay in $\sim 20\mu\text{s}$). In spite of the relatively high concentration, the S/N was still very low and it was necessary to signal average 10 000 experiments (taken at the rate of 100 per second) to obtain good kinetic traces.

Results and Discussion

Hydrated electrons rapidly react with *p*-bromobenzoate anions ($k(e_{\text{aq}}^- + \text{BrC}_6\text{H}_4\text{CO}_2^-) = 7.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)¹⁵ to eliminate bromide ions¹⁶ and to produce the *p*-carboxyphenyl radical which can be seen directly in steady-state ESR experiments.⁹ Presumably the reaction is



The yield of bromide ions attributed to reaction 1 in 1 mM deaerated bromobenzoate solution has been found to be 2.7.¹⁶ Since the observed yield is essentially identical with the value of 2.74 predicted by the model of Balkas et al.¹⁷ at a solute concentration such that $k[\text{S}] = 7.7 \times 10^{-6} \text{ s}^{-1}$, reaction 1 is quantitative. Production of the complementary carboxyphenyl radical was studied by examining the yield of benzoic acid produced in the presence of a high concentration of an appropriate hydrogen donor. The results described immediately below show that this yield is equivalent to that for the production of bromide. The optical spectroscopy following the pulse irradiation of these solutes shows, after the initial rapid increase in absorbances expected for the cyclohexadienyl radicals produced by reaction of OH radicals and H atoms (rate constants of $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $\sim 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively),^{18,19} a further increase which can be attributed to the formation of the *p*-carboxyphenyl adducts to the bromobenzoate, i.e.



Measurement of the period of this growth at a given bromobenzoate concentration allows k_2 to be determined. This work is described in the second section. In the final section the changes in the intensity of the ESR signals of *p*-carboxyphenyl radical are followed directly in time-resolved experiments which provide observations on the loss of these radicals and an absolute measurement of k_2 . The optical and ESR determinations confirm each other.

In the presence of other reactive solutes the *p*-carboxyphenyl radicals will be removed competitively. For example, in the presence of alcohols, which can act as hydrogen donors, benzoic acid is expected to be formed:

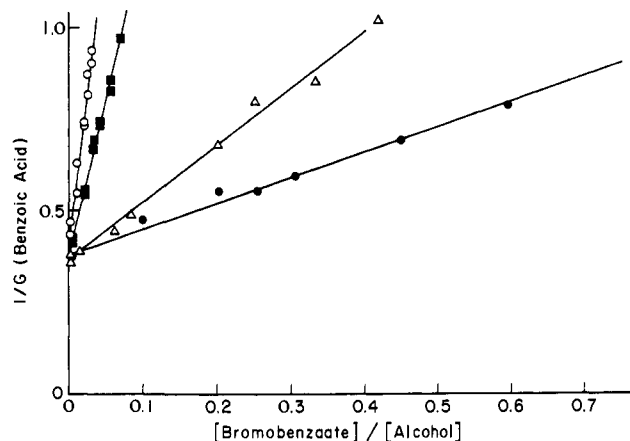


Figure 1. Competition plots of the yield for benzoic acid production as a function of the *p*-bromobenzoate to alcohol ratio: ●, isopropyl alcohol; ▲, ethyl alcohol; ■, methyl alcohol; and ○, *tert*-butyl alcohol. The common intercept of the lower three lines corresponds (cf. eq 4) to $G(e_{aq}^-) = 2.65$.



The rate constants for such abstraction reactions can be determined from the effects on the lifetime of the *p*-carboxyphenyl radical manifest in either the ESR or optical studies. The relative rate constants can be determined from competitive studies such as described in the first section or absolute values determined from effects on the lifetime of the carboxyphenyl radicals, as in the latter two sections. The results from these combined approaches (product analysis, optical pulse radiolysis, time-resolved ESR spectroscopy) leave little question but that one is studying the addition and abstraction reactions of phenyl radicals and that all of these reactions are, in fact, moderately rapid.

Product Analysis Studies. In the absence of an added H atom source, the radiolysis of a nitrogen purged bromobenzoate solution results in only a low yield of benzoic acid. This yield ($G = 0.21$ at a dose of 9×10^{17} eV/g and a bromobenzoate concentration of 1 mM) increases with dose and decreases with solute concentration. It appears to result largely from tertiary reactions of the carboxyphenyl radical with the radiation produced product. H abstraction from the bromobenzoate itself is probably unimportant. If an H atom donor such as isopropyl alcohol is added to the system, the benzoic acid yield increases as expected from simple competition between reactions 2 and 3 until a yield of 2.77 is reached in one experiment at an isopropyl alcohol to bromobenzoate concentration ratio of 200:1. Since this yield is, within experimental error, identical with the bromide yield and to the yield of electrons scavenged by 10^{-3} M bromobenzoate, it can be concluded that reaction 1 produces *p*-carboxyphenyl radicals quantitatively.

Results from studies of the dependence of the benzoic acid yields on the concentration of a number of added alcohols, [RH], are plotted in Figure 1 in the linear form expected from the competition between reactions 2 and 3, i.e.

$$\frac{1}{G(C_6H_5CO_2^-)} = \frac{1}{G(e_{aq}^-)} \left[1 + \frac{k_2[BrC_6H_4CO_2^-]}{k_3[RH]} \right] \quad (4)$$

The observed yields of benzoic acid have been corrected by subtracting the fraction of the background observed in the absence of alcohol which can be attributed to reactions other than reaction 3. These latter corrections are relatively small and are reasonably well made at concentrations sufficient to scavenge at least 40% of the phenyl radicals but still provide the principal systematic source of uncertainty in the relative

Table I. Rate Constants for Reaction of Carboxyphenyl Radicals

Solute	Absolute rate constants $\times 10^{-6} M^{-1} s^{-1}$		
	Product ^a analysis	Optical	ESR
Bromobenzoate	(8.4) ^a	7.4 ± 0.7^b	7.8 ± 0.8^b
Methyl alcohol	0.43 ± 0.04	0.4 ± 0.08	
Ethyl alcohol	2.4 ± 0.3	2.0 ± 0.5	
Isopropyl alcohol	5.2 ± 0.5	5.5 ± 1.0	6.2 ± 1.2
<i>tert</i> -Butyl alcohol	0.21 ± 0.04	0.32 ± 0.06	
Benzene		5 ± 2^c	

^a Rate constants measured relative to addition to bromobenzoate at an ionic strength of 0.003. Rate constant of $7.4 \times 10^6 M^{-1} s^{-1}$ assumed for this addition at zero ionic strength. Applying an ionic strength correction factor of 1.137 this value corresponds to a rate constant of $8.4 \times 10^6 M^{-1} s^{-1}$ at the experimental conditions. ^b Corrected to zero ionic strength; see Figure 3. ^c Benzene concentration taken as 0.020 M.

rate constants determined from the slopes and intercepts of plots of eq 4.

It is seen in Figure 1 that the linearity of the competition plots is reasonably good with a common intercept being observed for methyl, ethyl, and isopropyl alcohol. This intercept corresponds to a limiting benzoic acid yield of 2.65 ± 0.10 which is, as mentioned above, essentially identical with the yield of 2.74 expected for electron scavenging at 10^{-3} M bromobenzoate. The intercept observed for the experimental series with *tert*-butyl alcohol appears to be somewhat higher (corresponding to a limiting yield of only 2.5). Because of its comparative unreactivity, the studies with *tert*-butyl alcohol require very high concentrations of this solute where, as is shown in other studies, impurities in the alcohol reduce the lifetime of the electrons appreciably so that they no longer react quantitatively according to reaction 1. The relative rate constants for H abstraction determined from the data of Figure 1 are 0.051, 0.28, 0.62, and 0.025, respectively, for methyl, ethyl, isopropyl, and *tert*-butyl alcohol (referred to a unit rate constant for addition to *p*-bromobenzoate at an ionic strength of 0.003). These relative rate constants are estimated to be accurate to $\pm 10\%$ in the first three cases and to $\pm 20\%$ in the case of *tert*-butyl alcohol. In Table I these relative rate constants are placed in the absolute scale by reference to an absolute value of $8.4 \times 10^6 M^{-1} s^{-1}$ for the addition reaction as determined below. The relative rate constants for the H abstraction reactions reported in the spin-trapping studies of Janzen et al.^{6b} (1:2.6:9.2 for methyl, ethyl, and isopropyl alcohol) are reasonably in accord with the current information (1:5.6:12.9); so their conclusions as to the lower absolute rates must result from systematic problems, probably an excessively low rate constant for the referenced trapping reaction.

It is expected that in the presence of a large excess of benzene the *p*-carboxyphenyl radicals prepared by reaction 1 will preferentially add to the benzene to produce a phenyl substituted cyclohexadienyl radical which should be readily oxidizable by ferricyanide to biphenyl-4-carboxylic acid.²⁰ Irradiation of a benzene saturated (0.02 M) solution 5×10^{-4} M in bromobenzoate containing 10^{-4} M ferricyanide gave a biphenyl-4-carboxylic acid yield of 2.32 (± 0.13). Using rate constants of 3.7×10^9 and $1.4 \times 10^7 M^{-1} s^{-1}$ for reaction of e_{aq}^- with the ferricyanide and the benzene,^{21,22} it is calculated, respectively, that 8.2 and 6.2% of the electrons will be lost by reaction with these added solutes so that a yield of only 2.35 *p*-carboxyphenyl radicals is expected. The observed yield of biphenyl-4-carboxylic acid (2.32) agrees exceedingly well showing that addition of the *p*-carboxyphenyl radical to the benzene and the subsequent oxidation of the substituted cyclohexadienyl radical are both quantitative.

Optical Pulse Radiolysis Studies. The pulse irradiation of

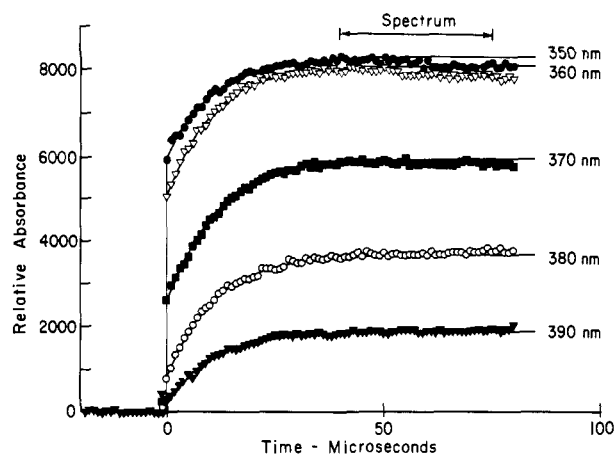


Figure 2. Absorbance changes observed for a 10 mM *p*-bromobenzoate solution at pH 7 purged with N_2 . The initial increase results from the reactions of H atoms, OH radicals, and e_{aq}^- which should all be complete within 1 μ s. A common period of 7.7 μ s was observed for the growth in absorption observed after the initial increase. This growth is attributed to the formation of the *p*-carboxyphenyl adduct to the bromobenzoate. The upper spectrum in Figure 3 corresponds to the data averaged over the indicated 40–75- μ s interval after the pulse.

a 10^{-2} M solution of bromobenzoate (pH 7, N_2 purged) shows, on the microsecond time scale, an initial increase in optical absorption at wavelengths less than ~ 380 nm. This increase presumably reflects, for the most part, the rapid addition of H and OH to the bromobenzoate where reaction should be complete within several tenths of a microsecond. Reaction of electrons with the bromobenzoate occurs on this same time scale so that this initial absorption will also manifest any carboxyphenyl radicals present. Following this initial absorption a slower growth occurs on the 10- μ s time scale, as is illustrated by the data of Figure 2. This additional absorption is attributed to the formation of substituted cyclohexadienyl radicals by the addition of the *p*-carboxyphenyl radicals to the bromobenzoate. As is illustrated in Figure 2, the relative amounts of the initial and delayed changes vary with wavelength but the growth period for the latter is wavelength independent. Above ~ 380 nm only the carboxyphenyl adduct absorbs significantly.

The total spectrum observed at 40–75 μ s after the pulse is illustrated by the solid circles in Figure 3 (spectrum 1). The contributions from the OH radical and H atom adducts determined from similar experiments on N_2O saturated solutions are also included (spectra 5 and 6 respectively).²³ By subtracting the latter from the observed spectrum a spectrum attributable to the cyclohexadienyl radicals produced in reaction 2 is obtained. This resultant spectrum is labeled 3 in Figure 3 and has a broad maximum at ~ 365 nm with an extinction coefficient of $3300 \text{ M}^{-1} \text{ cm}^{-1}$. This extinction coefficient is based on a yield of *p*-carboxyphenyl radicals of 3.07 as calculated for 10^{-2} M bromobenzoate from the relation given by Balkas et al.¹⁷ It is noted that, compared with cyclohexadienyl and hydroxycyclohexadienyl radicals which have maximum ~ 320 nm and no significant absorption above 350 nm, the spectra of the H and OH adducts of bromobenzoate are shifted considerably toward the red. The shift in the spectrum of the *p*-carboxyphenyl adduct is even more pronounced as is seen quite readily in Figure 3. This shift makes it possible to isolate reaction 3 spectroscopically as is seen very well in Figure 2.

The spectral data observed during the period 0.5–2.5 μ s after the pulse are given by the triangles in Figure 3 (dashed curve, spectrum 2). At wavelengths above ~ 360 nm the observed spectrum agrees well with spectrum 4 calculated by summing the contributions from the H and OH adducts and an addi-

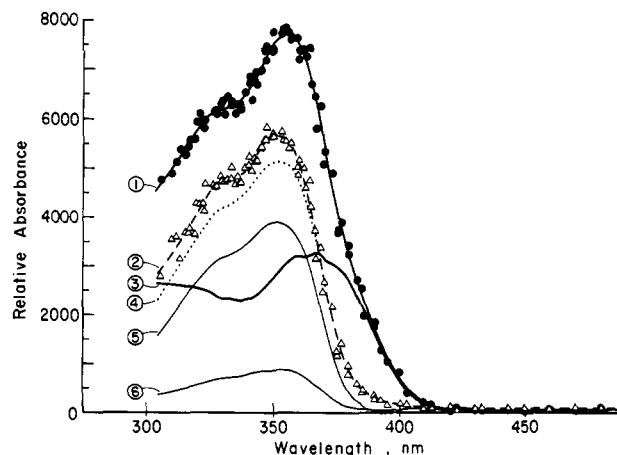


Figure 3. The absorption spectra observed (1) (\bullet) 40–75 μ s and (2) (Δ) 0.5–2.5 μ s after the pulse irradiation of a 10 mM *p*-bromobenzoate solution. The contributions from H and OH addition (cf. note 23) are indicated by spectra 5 and 6. The difference between 1 and the sum of 5 and 6 is given by spectrum 3 and attributed to the *p*-carboxyphenyl adducts to *p*-bromobenzoate. Spectrum 4 gives the spectra expected at 1.5 μ s from the sum of 5, 6, and 13% of 3.

tional 13% of the phenyl adduct, as is expected to be developed at the time of these observations. At lower wavelengths the observed absorption is somewhat more intense than expected from the synthetic spectrum indicating a contribution $\sim 500 \text{ M}^{-1} \text{ cm}^{-1}$ over the region 320–350 nm from the *p*-carboxyphenyl radical. The intercomparisons involved are, however, complicated and the differences noted can possibly be an artifact emphasized by small differences in the absolute extinction scales for the individual contributions (particularly that for the OH adducts). Cercek and Kongshaug³ attributed bands in the region of 260–280 nm observed in the irradiation of 10^{-4} M solutions of iodobenzene and *p*-bromophenol to phenyl and *p*-hydroxyphenyl radical. Maximum extinction coefficients of $630 \text{ M}^{-1} \text{ cm}^{-1}$ at 260 nm and $1905 \text{ M}^{-1} \text{ cm}^{-1}$ at 275 nm, respectively, were reported. They found very little absorption above 300 nm that could be attributed to these radicals. Any absorption of the *p*-carboxyphenyl radical in the 300–350-nm region almost certainly must result from a perturbation of the phenyl absorption by the carboxyl group. It is clear from the present study that such absorption cannot exceed $\sim 500 \text{ M}^{-1} \text{ cm}^{-1}$.

The observed pseudo-first-order rate constants determined from the growth period observed at 380 nm (open circles in Figure 4), when corrected for ionic strength effects (the solid circles in Figure 4), are linearly dependent on bromobenzoate concentration with the solid line in Figure 4 corresponding to a rate constant for reaction 2 of $7.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at zero ionic strength. Potential systematic errors are minor so that this value should be accurate to above the precision of the data analysis ($\sim 10\%$). The experimental rate constant observed at an ionic strength of 10^{-2} M (dashed line) is $9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

The addition of an H atom donor both decreases the reaction period and also the level of the absorption attributable to the various adducts, as expected from competition between reactions 2 and 3. The absolute rate constants for abstraction determined from such competitive experiments are given in column 3 of Table I. A relatively large error must be assigned to these rate constants since one can make the necessary measurements over only a small range of concentrations where the addition reaction contributes only 25–50%. The signals are consequently weak (adduct radical concentration of 10^{-6} M and absorbances of 0.004). Attempts to circumvent the problem by increasing the pulse intensity were frustrated by an increased contribution from the annihilation of phenyl radicals

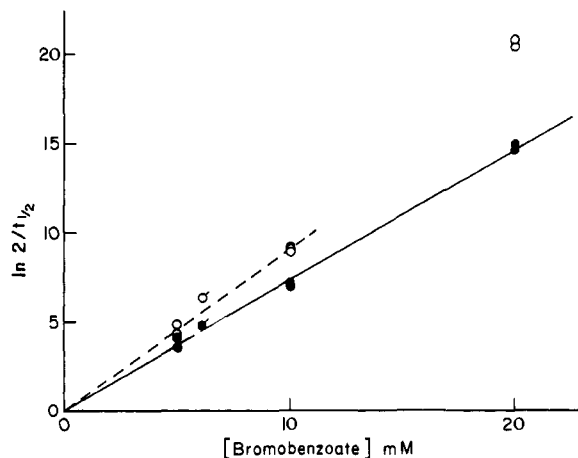


Figure 4. Pseudo-first-order rate constants for the addition of *p*-carboxyphenyl radicals to *p*-bromobenzoate: data as observed (O) optically and (O') by time resolved ESR spectroscopy. The corresponding solid symbols are after correction for ionic strength effects (cf. text). The solid line corresponds to $k_2 = 7.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Each point is the average of three-five measurements in separate series of experiments.

by reaction with alcohol radicals. These experiments, in fact, showed that the changes in the second-order processes resulting from the replacement of cyclohexadienyl radicals by alcohol radicals have reasonably important effects on the interpretation of the competitive data in these pulse experiments. In spite of this difficulty the optical data do show that the rates for reaction of carboxyphenyl radicals with the alcohols are of the magnitude indicated. We estimate a possible error of $\sim 20\%$ in these optically measured values of the abstraction rate constants.

One experiment was carried out on a benzene saturated solution using 0.5 mM bromobenzoate as the carboxyphenyl source. Again one observes at, for example, 315 nm an immediate increase in absorption attributable to the OH addition and a slower growth resulting from the production of the *p*-carboxyphenyl adducts of benzene. At wavelengths above 350 nm only absorption due to the latter is seen. The observed absorption is, however, considerably weaker than in the case of the bromobenzoate. The growth period was found to be 7 μs which, assuming a saturation concentration of 20 mM, corresponds to a rate constant of $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the addition rate. While this value should be very close to the actual rate constant, it, in fact, represents a lower limit since the actual benzene concentration may be somewhat less than that of saturation.

Time-Resolved ESR Experiments. The *p*-carboxyphenyl radical exhibits a nine-line ESR spectrum characterized by one pair of protons with a 17.06-g coupling constant and a second pair with a 5.88-g coupling constant ($g = 2.00224$).⁹ Examination of the central line for solutions 0.5 mM in *p*-bromobenzoic acid at pH 11.3 both with and without 23 mM isopropyl alcohol (ionic strength 0.014) gives the time dependence illustrated by the data of Figure 5. It is quite clear from these data that the addition of the alcohol reduces the lifetime of the *p*-carboxyphenyl radical appreciably. cursory examination of the lower curve in Figure 5 indicates a half-life of $\sim 8 \mu\text{s}$ which corresponds to a rate constant $\sim 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the abstraction reaction. Corrections, however, must be applied to this estimate for the relaxation processes and for the decay observed in the solution without alcohol.

Because of the relatively high doses employed in these experiments the data in the absence of alcohol represent the combined loss of phenyl radicals resulting both from reaction 2 and from reactions of the phenyl radical with other radicals. The latter are, in fact, the predominant source of the decay

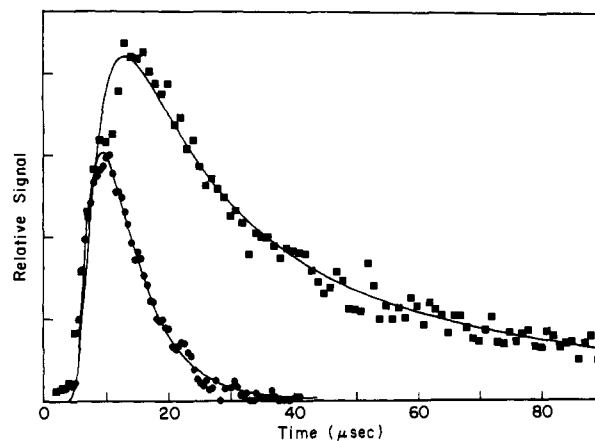


Figure 5. Curves of ESR absorption of the central line of *p*-carboxyphenyl radical as a function of time after the radiolysis pulse for solutions containing (■) 0.5 mM *p*-bromobenzoic acid and (●) both 0.5 mM *p*-bromobenzoic acid and 23 mM isopropyl alcohol. These studies were carried out at pH 11.3 and an ionic strength of 0.014. Solid curves are calculated by integration of the Bloch equations as described in the text. Data represent the average of 10 000 experiments.

observed at 0.5 mM bromobenzoate at the doses used. Increasing the bromobenzoate concentration to 6.1 mM accentuates the importance of reaction 2 and results in data similar to those found with the added alcohol. The experimental data were analyzed by comparing them with results from numerical integration of the Bloch equations, taking into account the second-order recombination process, the pseudo-first-order addition to the bromobenzoate, and the pertinent relaxation periods ($T_1 = 8 \mu\text{s}$; $T_2 = 2 \mu\text{s}$).¹³ Effect of magnetic inhomogeneities was also taken into account.²⁴ All data were taken at the same dose per pulse to allow correction for the second-order reaction.²⁵ The calculations were carried out iteratively with the initial estimate of the rate constant for reaction 2, as determined at the higher concentration, used to correct for this contribution at the lower concentration. Convergence was rapid. The data at the higher concentration, where the second-order reaction influences the calculation to only a minor extent, can be fitted quite well with k_2 taken as $1.03 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Correction for ionic strength effects gives a value of $7.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant for addition of *p*-carboxyphenyl radicals to bromobenzoate anion at zero ionic strength. This value is estimated to be accurate to $\sim 10\%$.

A rate constant $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the addition reaction is consistent with the observation by Zemel and Fessenden⁹ that maximum steady-state ESR signals of phenyl radicals produced from the haloaromatics are observed in the solute concentration region of 0.5–1 mM. At low solute concentrations the steady-state radical concentrations will be limited by second-order processes and depletion effects and at high solute concentrations by addition to the radical source. In the latter case the radical concentration will be inversely proportional to the solute concentration. As this concentration is increased, the radical concentration will increase until depletion becomes unimportant, level off, and then decrease again as the addition reaction takes over. Addition becomes dominant at concentrations $[S]$ above $2(k_R P / k_2)^{1/2}$ where P is the radical production rate in M s^{-1} and k_2 and k_R are the addition and combination constants. In a typical steady-state ESR experiment with $P \sim 0.01 \text{ M s}^{-1}$ the radical concentration controlled by combination processes should be $\sim 2 \times 10^{-6} \text{ M}$. With $k_2 = 8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ the steady-state concentration will be reduced by a factor of 2 at a solute concentration of 10^{-3} M and will decrease very rapidly at still higher concentrations. In the steady-state experiments one therefore expects a maximum signal in the region of 0.5–1 mM, as is observed.

The data for five solutions containing concentrations of isopropyl alcohol up to and including 23 mM were fitted similarly taking into account both the second-order decay of the phenyl radicals and the addition to the bromobenzoate. The rate constant for H abstraction reaction was determined from the slope of a plot of pseudo-first-order rate against concentration of alcohol to be $6.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This value corresponds to a half-life for the reaction of $4.9 \mu\text{s}$ for the 23 mM solution or $\sim 40\%$ less than indicated by the more casual estimate given above. In this case, as in the optical study, the change in complementary radicals produced as the result of abstraction from the isopropyl alcohol causes a change in the second-order processes and introduces a small additional uncertainty in the interpretation of the data.²⁵ The value given by this determination is probably slightly high and is estimated to be accurate to only $\sim 20\%$.

Conclusions

The summary of the rate constant data given in Table I shows values which are internally consistent within limits of interpretation of the data. The product studies show that the reactions assumed in treating the kinetics are quantitative so that there can be little doubt about the interpretation of the kinetics. The rate constants for the addition of the *p*-carboxyphenyl radical to bromobenzoate and to benzene are, therefore, clearly in the range $5\text{--}10 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and addition of phenyl radicals to most aromatic systems is expected to be characterized by a value of this magnitude. Such a rate constant is a factor ~ 5 greater than that suggested by Lorand and co-workers⁷ for addition of phenyl radicals to benzene and a factor ~ 50 greater than that concluded by Janzen and co-workers from their spin trapping studies.⁶ It is lower by a factor ~ 5 than the rate constant obtained by Cercek and Kongshaug for the addition of *p*-hydroxyphenyl radical to *p*-bromophenol but recent experiments in these laboratories²⁶ show that this latter difference is real, reflecting that at least small effects on the reaction rate can result from substitution on the radical. The fact that the *p*-hydroxy group increases the rate constant by only a factor of ~ 5 shows the substitution on phenyl cannot have any strong influence on the reaction rates and supports the argument used here that the reactivities of phenyl and *p*-carboxyphenyl should be very similar.

The hydrogen abstraction reactions of phenyl radicals are remarkably rapid. The ratio of the rate constants for the abstraction and the addition reactions is about the same as for similar reactions of OH radicals even though the latter react about three orders of magnitude more rapidly. The H abstraction processes are far more rapid than related abstractions by simple alkyl radical where rate constants are more characteristically $10\text{--}1000 \text{ M}^{-1} \text{ s}^{-1}$.²⁸ ESR studies show that the unpaired electron in the phenyl radical is in an orbital with $\sim 10\%$ s character, i.e., that phenyl is a σ and not a π radical.

The high reactivity toward addition and even more particularly that toward abstraction presumably reflect this σ character. Similar effects are observed for vinyl²⁹ and in CF_3 radicals³⁰ where the orbitals occupied by the unpaired electron also have a high degree of s character.

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References and Notes

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- (24) Because the central line which corresponds to a total spin of zero for both sets of protons was examined, effects of CIDEP should be limited to those produced by the difference in g factors between the phenyl radical and the other radicals (abstraction products and those produced by OH). These effects should be minor so that the ESR intensities should be describable by the Bloch equations.
- (25) It was assumed in the calculations that all second-order reactions had the same rate constants. The correction for the second-order reaction is probably underestimated since the optical data indicate the *p*-carboxyphenyl radical reacts somewhat more rapidly with the isopropyl alcohol radical than with the cyclohexadienyl radicals.
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