

methyl nitrate formed (equal to RCH_2COCH_3/RCH_2ONO_2) varies over almost a factor of ten. No explanation of this observation can be given. Neither methyl nitrate nor a methyl nitrate precursor is disappearing by reaction with acetone or *tert*-butyl nitrite; otherwise complete accountability of *tert*-butoxy radicals would not be obtained.

(f) **Influence of Structure on the Excited Radical Effect.**—The α quantities for isopropoxy and *tert*-butoxy radicals formed by photolysis of some peroxides (Table IV) differ but slightly. A small

TABLE IV

α VALUES OF ALKOXY RADICALS FORMED BY PHOTOLYSIS OF SOME DIALKYL PEROXIDES

Peroxide pressure, 23.5 mm.; nitric oxide pressure, 15 mm.;
 λ 2537 Å., T , 26°

Peroxide	α -C ₃ H ₇ O	α -C ₄ H ₉ O
Diisopropyl	0.60	..
Di- <i>tert</i> -butyl	..	0.53
Isopropyl- <i>tert</i> -butyl	0.72	0.64

difference in α is consistent with available thermochemical data,²⁰ which indicates that the enthalpies of decomposition of the two species differ by less than 2 kcal./mole. The ratio of $\alpha_{\text{isopropoxy}}$ (from diisopropyl peroxide) to $\alpha_{\text{tert-butoxy}}$ (from di-*tert*-butyl peroxide) is the same as the ratio of $\alpha_{\text{isopropoxy}}$ to $\alpha_{\text{tert-butoxy}}$ (both from isopropyl-*tert*-butyl peroxide), showing that the relative α values of the two radicals are not primarily de-

(20) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959); N. W. Luft, *Z. Elektrochem.*, **60**, 94 (1956).

termined by the deactivation efficiency of the parent peroxide. The lifetime of the excited radical before decomposition is one factor surely important in determining the magnitude of α .

The tentative conclusion from this work is that ethoxy radicals from photolysis of ethyl-*tert*-pentyl peroxide do not decompose in the presence of an excess of nitric oxide—hence are not excited in the sense used in this paper. This result fits well with the observation by Wijnen²¹ that isopropoxy radicals from photolysis of isopropyl propionate are excited but ethoxy radicals from photolysis of ethyl propionate are not excited.

Conclusions.—In vapor phase photolysis of dialkyl peroxides with *sec*- or *tert*- (possibly not *prim*-) alkyl groups, consideration must be given to the formation of excited alkoxy radicals—excited in the sense that they decompose (but do not abstract hydrogen) at an abnormally high rate. This effect introduces complications which make difficult an exact interpretation of some previous work on *tert*-butoxy reactions based on di-*tert*-butyl peroxide as a photolytic radical source. Some of the quantitative conclusions^{4,5} are obviously rendered uncertain.

The observation of apparent collisional deactivation of excited *tert*-butoxy radicals suggests that the excited radical effect may not be important in the liquid phase.

Acknowledgments.—The author benefited from discussions with Dr. S. D. Cooley and Mr. W. E. Taylor. The author also remembers that Mr. R. W. Jarrett interpreted and calculated all the mass spectral data.

(21) M. H. J. Wijnen, *J. Am. Chem. Soc.*, **82**, 1847 (1960).

[CONTRIBUTION FROM THE RADIATION PHYSICS LABORATORY, ENGINEERING DEPARTMENT, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE]

Pulse Radiolysis of Aromatic Compounds

BY A. MACLACHLAN AND R. L. MCCARTHY

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Pulsed radiolysis of benzene, chlorobenzene, bromobenzene, toluene, *p*-xylene, anisole and mesitylene has led to the observation of transient absorptions. Product analysis, spectroscopic data and kinetic analysis indicate that the transients produced are free radicals, having a conjugated structure, derived from addition of reactive radicals to the parent aromatic compound. Bimolecular rate constants for the radical-radical reaction are calculated, and the rate of addition of phenyl radicals to chlorobenzene is estimated.

Introduction

Pulsed radiolysis has been shown to be a valuable technique for the production and observation of very reactive free radicals.^{1,2,3} Previous publications from this Laboratory have reported the kinetics of benzyl radical dimerization,¹ the dimerization and disproportionation of ketyl radicals from cyclohexanol and the kinetics of some peroxy radical reactions, including cyclohexyl peroxy and octene peroxy radicals.^{21,8} This paper sum-

marizes an investigation of the nature of the transients observed when various aromatic compounds are pulse radiolyzed. Kinetic order and detailed product analysis are used to make assignments of product structure and for the calculation of absolute rate constants.

Experimental

Materials.—Benzene was Mallinckrodt analytical reagent; toluene was Merck reagent grade; anisole, bromobenzene, biphenyl and bibenzyl were Eastman white label chemicals; *p*-xylene, iodobenzene and phenylcyclohexane were Matheson, Coleman and Bell chemicals; 4,4'-dichlorobiphenyl and bicyclohexyl were obtained from the Aldrich Chemical Company; cyclohexane was Eastman Spectro

(1) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960).

(2) R. L. McCarthy and A. MacLachlan, *ibid.*, (in press).

(3) R. L. McCarthy and A. MacLachlan, *J. Chem. Phys.* (in press).

ELUTION CHROMATOGRAPHY OF RESIDUE FROM IRRADIATED CHLOROBENZENE

Cut no.	Wt. (g.)	Average molecular weight	Elemental analysis, %				Comment
			Carbon	Hydrogen	Chlorine	Oxygen	
4	0.4128	250 \pm 10	66.25	4.00	26.69	2.87	Liquid
8, 9	.1099	418 \pm 18	57.65	4.20	White solid
10	.0406	397 \pm 18	White solid
13	.0603	486 \pm 25	White solid
15	.5508	499 \pm 25	59.75	4.46	35.71	0.27	Yellow solid
16	.4068	1045 \pm 100	60.45	4.15	35.21	0.36	Yellow solid

Grade. Iodine was Baker analyzed reagent grade; sodium thiosulfate was Mallinckrodt analytical reagent; argon was Linde high-purity-dry (99.995%); and oxygen was obtained from Airco.

Cobaltous chloride hexahydrate (Mallinckrodt analytical reagent) was dried in an oven and then dissolved in anhydrous 50% acetone–50% bromobenzene for experiments involving the effect of paramagnetic ions on the lifetime of the transient.

Chlorobenzene (Fisher Scientific Company) was purified by the method of Wu, Hammond and Wright.⁴ Ortho- and paradichlorobiphenyl were prepared by the ferric chloride catalyzed chlorination of biphenyl.⁵ The fractions boiling at 133° (33 mm.), essentially pure *o*-chlorobiphenyl, and 145° (30 mm.), essentially pure *p*-chlorobiphenyl, were used for calibration of the gas chromatograph.

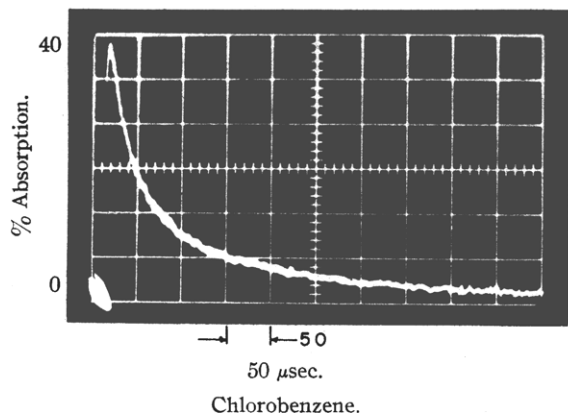


Fig. 1.—Transient absorption obtained by pulse radiolysis of oxygen-free chlorobenzene.

Analytical Techniques.—All products boiling up to approximately 350° were analyzed by gas-liquid chromatography (g.l.c.). Quantitative analyses were performed by comparison of peak heights or peak areas with those of known concentrations of standard compounds. The gas chromatograph used for this work was a Perkin–Elmer Model 154, equipped with a hydrogen-flame ionization detector and a 150-ft. Golay column “R.” This arrangement has sufficient sensitivity to quantitatively measure the biphenyl yields without preliminary evaporation, when the concentration of biphenyls in the radiation solution is greater than 0.002 *M*.

Elution chromatography was used to analyze the high-boiling residue obtained from the irradiated chlorobenzene. The column packing was Florisil obtained from the Burrell Corporation, and solvents were cyclohexane, 1% benzene–99% cyclohexane, 10% benzene–90% cyclohexane, pure benzene and other various concentrations of ethanol in benzene up to pure ethanol. One hundred and fifty ml. of pure chlorobenzene was irradiated after flushing with argon to a total dose of 3.2×10^{23} ev. The majority of the chlorobenzene was then removed by vacuum evaporation at 50°. The residue (3.45 g.) was then used for analysis. Cyclo-

hexane eluted the g.l.c. analyzable fraction very rapidly. Benzene–cyclohexane mixtures eluted a series of white solids of low melting point (50–100°). Benzene and ethanol and, finally, pure ethanol eluted a larger number of continuously higher melting solids with melting points ranging to 200°. Seventy-seven per cent. of the radiation residue was recovered from the elution chromatograph. Selected fractions of the residue were analyzed, as given in the table below.

Irradiation Procedure.—For product analyses the solutions were irradiated in the 100–150 ml. radiation cell previously described.⁶ All irradiations were performed with solutions that had been flushed for one-half hour with argon. The argon was presaturated with the appropriate solution when severe evaporation would result from the flushing.

Pulsed radiolyses were performed using a Linear Electron Accelerator with the apparatus previously described by the authors, using the photoelectric recording technique.^{1,2,3} The absorbed energy per pulse is approximately 5.4×10^{18} ev./ml.

Results

Transients Observed.—Transient absorptions were observed from all the aromatic compounds reported in Table I. The wave length and per cent. absorption are given.

TABLE I

SPECTRAL DATA ON AROMATIC TRANSIENTS

Compound	Wave length obsd., λ_{max}^a	Maximum absorption of transient (% incident light)
Benzene	3200	30
Toluene	3200	32
<i>p</i> -Xylene	3150	32
Mesitylene ^b	3200	30
Anisole	3400	31
Chlorobenzene	3500	43
Bromobenzene	3550	62

^a Transient analyses were always performed at the point of maximum absorption. ^b Pulsed as a mixture with 75% cyclohexane.

The radicals derived from most of the aromatic compounds listed in Table I react by second order kinetics. As an example, Fig. 1 shows the oscilloscope trace for the transient absorption observed when pure chlorobenzene is pulse radiolyzed, and Fig. 2 is the curve obtained when the reciprocal of the optical density is plotted *versus* time. Figure 3 presents the second order curves for the other aromatic compounds.

A rough absorption spectrum for the benzene transient was obtained by taking point-by-point optical density measurements as a function of wave length and is given in Fig. 4. The transient

(4) C. S. Wu, G. S. Hammond and J. M. Wright, *J. Am. Chem. Soc.*, **82**, 5386 (1960).

(5) R. L. Jenkins, R. McCullough and C. F. Booth, *Ind. Eng. Chem.*, **22**, 31 (1930).

(6) A. MacLachlan, *J. Am. Chem. Soc.*, **82**, 3309 (1960).

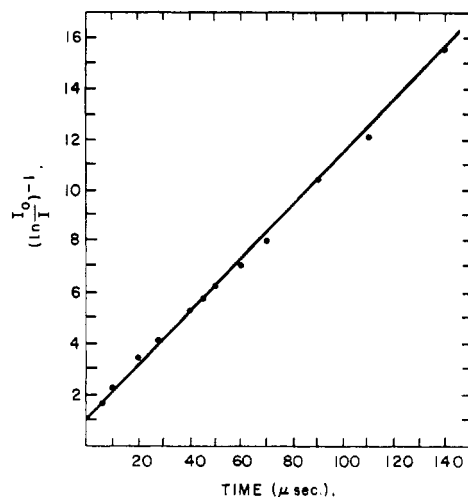


Fig. 2.—Plot of reciprocal optical density *versus* time, showing second order kinetics.

obtained from irradiated chlorobenzene was taken in the same manner and is also given in Fig. 4. Similar scans for the transients, obtained with the other aromatic compound, were performed, and no structure was detectable with the resolution available.

TABLE II

PRODUCTS OBTAINED FROM CHLOROBENZENE

Radiolysis at 25°		
Products	G-Yields ^a	(Iodine added) ^b
Benzene	1.12	0.091
Biphenyl	0.10	.021
<i>o</i> -Chlorobiphenyl	.32	.11
<i>m</i> -Chlorobiphenyl	.31	.16
<i>p</i> -Chlorobiphenyl	.31	.084
Iodobenzene	..	2.02

PRODUCTS OBTAINED FROM BENZENE

Radiolysis at 25°		
Products	G-Yields ^a	(Iodine added) ^b
Biphenyl	0.067	0.052
C ₁₂ Compounds	0.029	None
Iodobenzene	...	0.202

^a Dose for these runs was approximately 1×10^{21} ev./ml. Irradiations were performed with a 2-Mev. Resonant Transformer for these product isolations. One analysis, using products generated with the linear accelerator beam, yielded an identical product spectrum. ^b Solution maintained in contact with iodine during irradiation.

When mixtures of chlorobenzene and cyclohexane are irradiated with pulsed high-energy electrons, the transient absorption decreases with increasing cyclohexane concentration to the point that no absorption is detected when the cyclohexane concentration exceeds 25% by volume. The radical half-life remains constant at 28 ± 3 μ sec. Anisole did not yield a satisfactory straight line when the reciprocal of the optical density was plotted *versus* time.

Pulsed radiolysis of pure bromobenzene led to a complex absorption transient centered at 3500

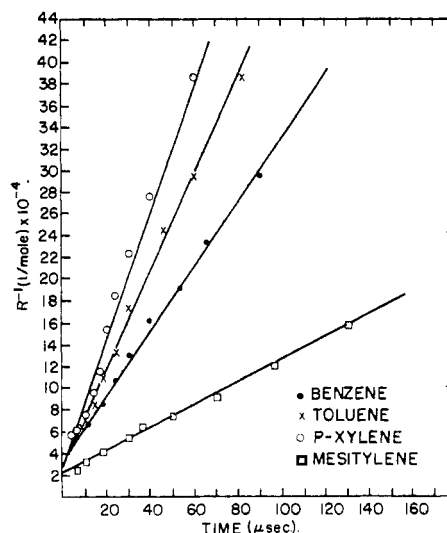


Fig. 3.—Plot of reciprocal radical concentration *versus* time for the aromatic hydrocarbon.

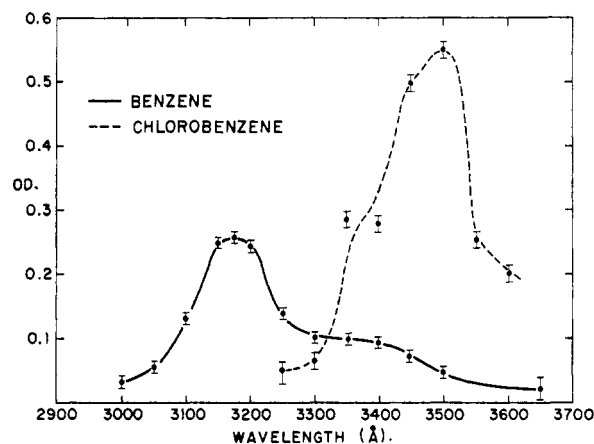


Fig. 4.—Rough absorption spectra of transients obtained from chlorobenzene and benzene.

A, which could be resolved into a rapid decay following second order kinetics ($\tau_{1/2} \cong 8$ μ sec.) and a very slow first order decay ($\tau_{1/2} = 1.9$ sec.). It seemed reasonable that a triplet state was responsible for this long-lived transient, and strong evidence for this conclusion was obtained when the addition of 5×10^{-3} *M* CoCl₂ to a mixture of acetone and bromobenzene shortened the lifetime by a factor of 100.

In the case of all aromatics studied, oxygen eliminates the short-lived transients.

Radiation Products.—Elucidation of the structures responsible for the observed transients requires a knowledge of the final products. Chlorobenzene and benzene were examined in the greatest detail. The G-yields for products of these irradiations are given in Table II.

The gas chromatographic technique used in this study was capable of analyzing any stable compound with a boiling point below 350°. This amounted to 18 and 26% of the residues from the irradiated chlorobenzene and benzene, respectively.

Infrared analysis of the fractions obtained by elution chromatography of the chlorobenzene residue indicated the presence of much unsaturation, aromatic rings and carbonyl groups. The carbonyl groups must be the result of post-oxidation of unsaturated structure, since the irradiations are carried out on deoxygenated samples.

Discussion and Conclusions

This study is concerned with identifying the transient species produced in aromatic systems by high-energy radiation and obtaining the rate constants describing their reactions. The experimental data consists of physical and chemical facts that must be considered in determining the transients' identity. They are

1. The kinetics of most of the transients are clearly second order, indicating radical-radical recombination.

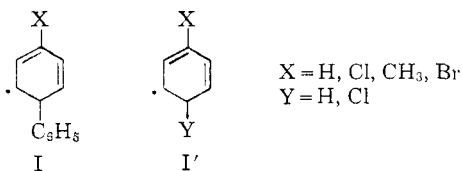
2. Chlorine, bromine and methoxy substituents on the aromatic ring shift the wave length of maximum absorption strongly to the red (Table I), hence the transient absorption cannot originate from the unsubstituted phenyl radical in all cases.

3. The long-lived transient obtained with bromobenzene is strongly quenched by added cobaltous ion, hence this absorption is attributed to a triplet rather than a free radical intermediate. The first order kinetics are also evidence for a triplet state.

4. Product analysis demonstrated that very complex reactions had occurred. Chlorobenzene yielded *o*-, *m*- and *p*-chlorobiphenyls, biphenyl, dichlorobiphenyls and benzene plus a very complex mixture of unsaturated high-molecular-weight compounds. Benzene yielded biphenyl and a mixture of phenylcyclohexadienes and dicyclohexadienes. Toluene reacted to form a very complex mixture of product, including bibenzyl and dimethylbiphenyls.

5. Irradiation of chlorobenzene and benzene in the presence of iodine yielded mainly iodobenzene. This result is taken as strong evidence that phenyl radicals are the primarily formed species.

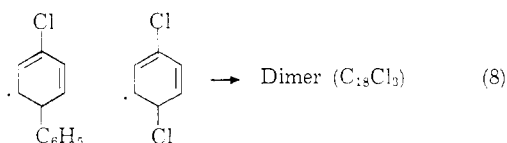
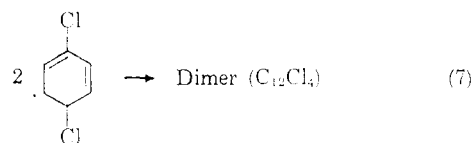
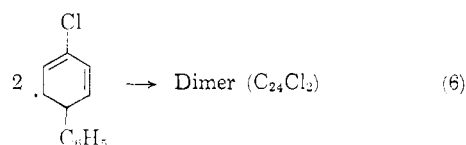
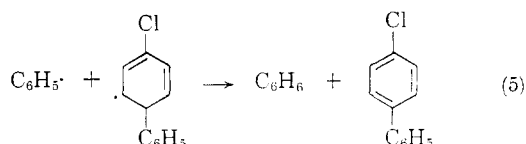
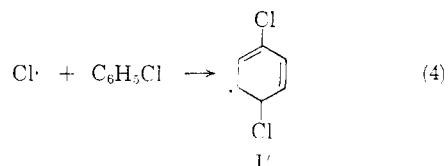
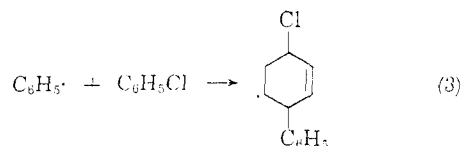
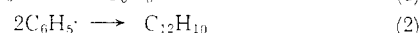
From a consideration of the previous data, it is believed that the observed transients are best explained by bimolecular reactions of radicals of the structures I and I'



Phenyl-type radicals are certainly present, but due to the large red shift in the ultraviolet spectrum for chlorobenzene, bromobenzene, and anisole, as well as the absence of dichlorobiphenyls, the conjugated structures I and I' are favored. It should be recognized that I and I' represent all possible *ortho*-, *meta*- and *para*-derivatives of the conjugated radical. The relative unimportance of the

biphenyl fraction is also strong evidence for the presence of these more complex radicals.

It is proposed that the radical structures I and I' are derived from reactions such as those shown below. Chlorobenzene is used as an example. The reactions are expected to be similar for all the aromatic systems encountered in this work.



Further confirmation of reactions 3 and 4, *e.g.*, rapid addition of reactive radicals to the parent compound, was obtained by examination of the fractions from elution chromatography of the chlorobenzene residue. Molecular weight determination (see Experimental) indicate that the products, non-analyzable by gas chromatography, contain three to four C₆ groupings and two or more halogen atoms. The steadily increasing molecular weights are expected because of the high conversions (~2%) used to obtain the chromatographic sample. Infrared spectra of the various fractions showed carbonyl bands, which must result from post-oxidation. The initially formed products are thus sensitive to both further molecular weight increases by radical addition and by oxidation. The early elution chromatographic cuts have molecular weights of approximately 400. Elution chromatography will separate the products in the order of their polar character, and thus the absolute

values of the molecular weights has little value, since they are averages. This is shown by a gas chromatographic analysis of Cut No. 4, where 67% is made up of biphenyl, dichlorobenzene and chlorobiphenyls, and the remainder does not elute, yet the average molecular weight is 250. Correcting for the "analyzable" part of Cut No. 4, the remaining material has a calculated molecular weight of approximately 400. The carbon, hydrogen, chlorine analysis of selected cuts lends further support to the character of the products, since the average analysis agrees with the product being made up of increments of chlorobenzene residues. Gordon, *et al.*,⁷ and, more recently, Gäumann⁸ have presented strong evidence of a similar mechanism occurring in electron-irradiated benzene.

Iodine is unable to reduce the chlorobiphenyl yields by more than a factor of three, suggesting that at least some of the chlorobiphenyls are formed by very rapid processes, perhaps in spurs. Benzene formation from irradiated chlorobenzene is strongly retarded by iodine, serving as evidence that phenyl radicals are the benzene precursors. The biphenyl produced from chlorobenzene is probably the result of phenyl radical combination, since it, too, is reduced by at least a factor of five in the presence of iodine. The primary radical generated from both benzene and chlorobenzene is a phenyl radical and that from toluene, *p*-xylene and mesitylene is a substituted phenyl radical formed by removal of a hydrogen atom.

Kinetics.—The previous discussion has been concerned with identification of the transients. It will now be shown that it is possible to obtain an estimate of the absolute rate constants from the data.

The radicals derived from chlorobenzene, benzene, toluene, *p*-xylene and mesitylene react by second order kinetics as shown in Figs. 2 and 3. Anisole and bromobenzene present exceptions to the second order kinetics obtained with the other aromatics. No product analysis was attempted in anisole, but it seems reasonable that two different radical species would be formed from this molecule. Removal of ring hydrogen atoms or the methoxy group would yield phenyl-type radicals, while rupture of the methyl oxygen bond of the methoxy substituent would yield the known phenoxy radical.⁹ In bromobenzene a fast decay approximating second order kinetics with a half-life of about 8 μ sec. was superimposed on the long-lived first order transient.

For calculation of absolute rate constants, chlorobenzene will again serve as a model, and the conclusions reached will be extended to include the other aromatic systems. Iodine trapping to form iodobenzene with a $G = 2.02$ is one possible way to obtain an estimate of the total number of radicals formed, $G(R\cdot)$. A chlorine atom must accompany the formation of the phenyl radical, and thus the true initial radical yield is 4.04 per

100 ev. absorbed. A second approach to calculating initial radical yield lies in a consideration of the amount of high-boiling residue formed and its structure as deduced from the end-product analysis. Chlorobenzene yields 1.67 g. of high-boiling residue for a total irradiation dose of 1.51×10^{23} ev. Gas chromatography accounted for only 17% of this residue, with the rest being assigned to higher-molecular-weight materials. From the mechanism proposed it would be expected that the compounds which make up the residue contain on the average three C₆ rings and three chlorine atoms, for an average molecular weight of 338. The number of moles of product is 4.1×10^{-3} , or 8.2×10^{-3} moles of radicals are formed, since two radicals combine to form the product. The radical G -yield calculated this way is 3.3. Benzene and biphenyls are also formed, but due to the excellent second order kinetics obtained, it is not certain that they contribute to the observed radical yield. For the calculation of the rate constants these products will be neglected, and their possible contribution will be considered as an uncertainty in the values of the rate constants. Table III lists the radical G -yields calculated using arguments based on the total weight and composition of the residue as presented for chlorobenzene. Where iodine trapping was used, this method of estimating the G -yield is included for comparison. The agreement between these two independent methods is quite encouraging for the two cases studied.

TABLE III

Compound	Total wt. of residue ^a	Assumed, b mol. wt.	Dose e.v. $\times 10^{-22}$	$G(R\cdot)$ calcd. c	$G(R\cdot)$ i ₂
Benzene	0.13	~272	1.40	$0.3 \pm 25\%$	0.4
Chlorobenzene	1.67	~338	1.51	$3.3 \pm 20\%$	4.0
Anisole	0.23	~334	1.88	$0.4 \pm 25\%$..
Toluene	0.17	~300	1.51	$0.5 \pm 25\%$..

^a Each compound received approximately the same total dose. Corrections for dose variation are included in the $G(R\cdot)$ calculation. Weight of products identified by g.l.c. were subtracted before calculation of $G(R\cdot)$ calcd. ^b As described in text. ^c This is the $G(R\cdot)$ used for the calculation of rate constants.

In determining the rate constants for these reactions consideration must be given to the significance of radical reactions occurring during the beam pulse and during the dead period of 6 μ sec. following the pulse. During the 5 μ sec. beam pulse a simplified expression for the rate of production of radicals is

$$\frac{dR\cdot}{dt} = PG - k_2(R\cdot)^2 \quad (1)$$

where R is the radical concentration, P is the electron-beam power absorbed, G is the 100-ev yield of radicals and k_2 is the second order rate constant for radical decay. After the beam is turned off, the second term of eq. 1 accounts for the kinetics. Using the total radical yields given in Table III, the problem is one of integrating eq. 1 over the 5- μ sec. beam pulse in order to obtain a

(7) S. Gordon, A. R. Van Dyken and T. F. Doumani, *J. Phys. Chem.*, **62**, 20 (1958).

(8) T. Gäumann, *Helv. Chim. Acta*, **44**, 1337 (1961).

(9) G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

k_2 that is consistent with the observed transient kinetics and the total number of radicals formed. The rate constants obtained in this manner are presented in Table IV. The probable error in their values from all recognized sources is estimated to be no more than a factor of 2. These errors arise from two main sources, *e.g.*, dosimetry and timing errors and uncertainty associated with the assignment of a total $G(R\cdot)$.

TABLE IV
RATE CONSTANTS FOR AROMATIC TRANSIENTS^a

Compound	Rate constant (l./mole sec.)
Chlorobenzene	3.0×10^8
Toluene	4.5×10^9
Benzene	2.8×10^9
<i>p</i> -Xylene	7.2×10^9
Mesitylene	1.0×10^9

^a It should be emphasized that these rate constants are not for a single substance but, as already pointed out in eqs. 5 through 8, are representative of combination reactions for all possible second order reactions of very similar conjugated radicals.

Using the same method of theoretically calculating rate constants as described in previous work,¹⁰ it is calculated that the diffusion-controlled rate constants for the reactions studied are close to 3×10^{10} l./mole sec. It appears that none of the reactions investigated are purely bimolecular diffusion-controlled reactions, although some approach this rate. Since measurements on other systems³ and theoretical considerations imply that no activation energy (<1 kcal./mole) is required for radical-radical reactions, we conclude that for these radicals a steric factor of approximately 10^{-1} to 10^{-2} is involved.

Phenyl Radical Reactions.—While the principal conclusion of this paper supports the rapid addition of primarily formed phenyl radicals to the parent aromatic compounds forming highly optically absorbing conjugated radicals, it is important

to consider that phenyl radicals are formed first. This phenyl radical addition to the parent aromatic compound is extremely fast, since it competes favorably with radical-radical reaction. An estimate of addition rate constant may be obtained as follows: Addition is expressed by

$$-\frac{d\varphi}{dt} = k_1[A][\varphi]$$

where $[\varphi]$ is the phenyl radical concentration, $[A]$ is the parent aromatic compound concentration, and k_1 is the bimolecular addition rate constant. Competing with this process are radical-radical reactions, *e.g.*

$$-\frac{dR\cdot}{dt} = k_2[R\cdot]^2$$

where k_2 is the bimolecular rate constant as calculated in Table IV. Taking chlorobenzene as an example, with $k_2 = 3 \times 10^8$ l./mole sec., and with a radical concentration after completion of the beam pulse of 4×10^{-4} M, the initial rate of the dimerization reaction is 48 moles/l. sec. To compete as favorably as it does and at the same time yield some biphenyl, the addition reaction will have to be about four times as fast as the dimerization reaction. Choosing the initial phenyl radical concentration as 4×10^{-4} M (actually a sum of phenyl radicals and chlorine atoms) and with the concentration of chlorobenzene of 9.85 M, the bimolecular addition rate constant k_1 is 4.8×10^4 l./mole sec.

It is believed that this estimate of the addition rate constant is probably not grossly in error, since if the addition were much faster then no diphenyl or benzene would be formed, and if it were much slower, biphenyl would be a much more significant fraction of the total product.

Acknowledgments.—The authors wish to thank V. F. Hanson, R. P. Schwenker, and J. M. White for their aid in the performance of these experiments.

(10) J. Waite, *J. Chem. Phys.*, **32**, 21 (1960).