(17) Publications about other recently developed noncyclic ligands: (a) D. Ammann, R. Bissig, M. Güggi, E. Pretsch, and W. Simon, *Helv. Chim. Acta*, **58**, 1535 (1975); (b) R. Büchi and E. Pretsch, *ibid.*, **58**, 1573 (1975); (c) N. N. L. Kirsch and W. Simon, *ibid.*, **59**, 357 (1976).

(18) W. D. Curtis, D. A. Laidler, J. F. Stoddart, and G. H. Jones, *J. Chem. Soc., Chem. Commun.*, 833, 835 (1975).

(19) IUPAC names of the compounds investigated: ligand I = 1,11-bis(8-quinolinyloxy)-3,6,9-trioxaundecane; ligand II = 2,6-bis(8-quinolinyloxymethyl)pyridine; ligand IV = [2.2.1$_{Py}$]diamide = 1,12-dioxo-2,11-diaza-5,8,21,24-tetraoxa[12.8^{2,11}](2,6)pyridinophane; ligand V = [2.2.1$_{Py}$] = 2,11-diaza-5,8,21,24-tetraoxa[12.8^{2,11}](2,6)pyridinophane (nomenclature of IV and V according to F. Vögtle and P. Neumann, *Tetrahedron*, **26**, 5847 (1970)).

(20) R. J. Dann, P. P. Chiesa, and J. W. Gates, *J. Org. Chem.*, **26**, 1991 (1961).

(21) W. Baker, K. M. Buggle, J. F. W. McOmie, and D. A. M. Watkins, *J. Chem. Soc.*, 3594 (1958).

(22) Chromatographic separation of complexes of I yields this ligand in high purity as a crystalline material with mp 75 °C. Personal communication by Dr. R. Klink, Merck AG, D-6100 Darmstadt.

(23) In view of this preparation technique see also J. Petranek and O. Ryba, *Collect. Czech. Chem. Commun.*, **39**, 2033 (1974).

(24) H. L. Schläfer, "Komplexbildung in Lösung", Springer, Berlin, 1961, Chapter 8.

(25) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(26) (a) R. Winkler, Thesis, Göttingen-Vienna, 1969; (b) K. Bräuer and H. Strehlow, *Z. Phys. Chem. (Frankfurt am Main)*, **17**, 346 (1958).

(27) (a) M. Eigen and L. De Maeyer in "Techniques of Organic Chemistry", Vol. VIII/2, A. Weissberger, Ed., Wiley, New York, N.Y., 1963, Chapter 18; (b) R. Rigler, C. R. Rabl, and T. M. Jovin, *Rev. Sci. Instrum.*, **45**, 580 (1974); (c) C. R. Rabl in "Technische Biochemie", Vol. 71, Dechema Monographien, H. J. Rehm, Ed., Verlag Chemie, Weinheim, 1973, p 187.

(28) D. Riesner, A. Pingoud, D. Boehme, F. Peters, and G. Maass, *Eur. J. Biochem.*, **68**, 71 (1976).

(29) Log of equilibrium constant Mg^{2+}/8-hydroxyquinoline: (a) in aqueous solution extrapolated to ionic strength at 25 °C, log K = 4.74; (b) in a 1:1 mixture of H_2O and dioxane (v/v) at 25 °C, log K_1 = 6.38, log K_2 = 5.43. 8-Methoxyquinoline forms complexes of smaller stability in aqueous solutions (medium: 0.1 M ionic strength at 25 °C): Cd^{2+}, log K = 1.3; Ni^{2+}, log K = 2.0; Zn^{2+}, log K = 1.6 (L. G. Sillén and A. E. Martell, Ed., "Stability Constants of Metal-Ion Complexes", The Chemical Society, London, 1964).

(30) (a) M. Eigen and G. Maass, *Z. Physik. Chem. (Frankfurt am Main)*, **49**, 163 (1966); (b) H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure Appl. Chem.*, **20**, 93 (1969); (c) Abbreviations: NTA = nitrilotriacetic acid; EDTA = ethylendiaminetetraacetic acid.

(31) (a) M. Eigen and R. Winkler, *Neurosci. Res. Prog. Bull.*, **9**, 330 (1971); (b) R. Winkler, *Struct. Bonding (Berlin)*, **10**, 1 (1972).

(32) M. Eigen, *Q. Rev. Biophys.*, **1**, 3 (1968).

(33) (a) E. Grell, Th. Funck, and F. Eggers in "Molecular Mechanisms of Antibiotic Action on Protein Biosynthesis and Membranes", E. Muñoz, F. Garcia-Ferrándiz, and D. Vazquez, Ed., Elsevier, Amsterdam, 1972, p 646; (b) E. Grell and Th. Funck, *J. Supramol. Struct.*, 307 (1973).

(34) S. W. Kuffler and J. G. Nichols, "From Neuron to Brain", Sinauer Associates, Sunderland, Mass., 1976, Chapter 6.

(35) M. Kirch and J. M. Lehn, *Angew. Chem.*, **87**, 542 (1975).

(36) Detailed paper in preparation.

(37) 8-Hydroxyquinoline *alone* induces a small depolarization.

(38) Heart cells of 1- to 2-day old Wistar rats were isolated by trypsination as described by Harary and Farley (*Exp. Cell Res.*, **29**, 451 (1963)). Cell culturing was performed in a modified nutrient medium SM 20 (W. Halle and A. Wollenberger, *Am. J. Cardiol.*, **25**, 292 (1970)).

A Quantitative Study of the Photostimulated Reaction of Iodobenzene with Diethyl Phosphite Ion[1]

Shmaryahu Hoz and Joseph F. Bunnett*

Contribution from the University of California, Santa Cruz, California 95064.

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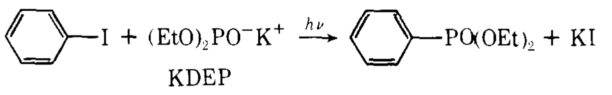
Abstract: The photostimulated reaction of iodobenzene with potassium diethyl phosphite (KDEP) in Me_2SO solution to form diethyl phenylphosphonate occurs with raw quantum yields at 313 nm considerably in excess of unity, frequently 20–50. Reaction rate is proportional approximately to the 0.84 power of light intensity. The dependence of quantum yield on KDEP concentration may be interpreted either on the basis that the photons absorbed by iodobenzene or the photons absorbed by a charge-transfer complex of iodobenzene with diethyl phosphite ion are responsible for initiation. Each of these alternatives is compatible with a different initiation mechanism. The quantum yield under conditions such that all the light is absorbed is independent of iodobenzene concentration. These facts are consistent with a radical chain mechanism with initiation as in steps 8 and 9, 8 and 10, or according to Scheme II, propagation according to Scheme I, and termination mainly via step 16 or 17 with a minor contribution from step 18.

In liquid ammonia solution, iodobenzene undergoes facile photostimulated reaction with diethyl phosphite ion to form diethyl phenylphosphonate[2] (eq 1).


(1)

This reaction is one of a family of photostimulated nucleophilic substitution reactions of unsubstituted phenyl halides and related substrates. Other nucleophiles that behave similarly are arenethiolate ions,[3] ketone enolate ions,[4,5] picolyl anions,[6] and the enolate ion of *tert*-butyl acetate.[7]

All these reactions are believed to occur by the $S_{RN}1$ mechanism. This mechanism, which involves radical and radical anion intermediates and electron transfer steps, was first proposed for certain nucleophilic substitutions at saturated carbon by Kornblum[8] and Russell[9] and their associates. Kim and Bunnett[10] recognized it as a mechanism of aromatic substitution in 1970, and proposed the symbol $S_{RN}1$. The propagation steps of the mechanism are represented, for the reaction of present interest, in Scheme I.

Scheme I

$$[PhI]^-\cdot \xrightarrow{k_2} Ph\cdot + I^- \qquad (2)$$

$$Ph\cdot + (EtO)_2PO^- \xrightarrow{k_3} [PhPO(OEt)_2]^-\cdot \qquad (3)$$

$$[PhPO(OEt)_2]^-\cdot + PhI \xrightarrow{k_4} PhPO(OEt)_2 + [PhI]^-\cdot \qquad (4)$$

A radical chain mechanism also must have initiation and termination steps, - but for the $S_{RN}1$ mechanism there has been little evidence as to what they are. For light-stimulated reactions, initiation has usually been represented as a photostimulated electron transfer from nucleophile to substrate, either in a charge-transfer complex or by photoejection and then electron recapture.[2-6] In that case the substrate radical anion would enter the propagation cycle at step 2. An alternative possibility is initiation by photolysis of the C–I bond,[11,12] forming phenyl radical which enters the cycle at step 3.

A quantitative study of the reaction of iodobenzene with diethyl phosphite ion was undertaken for the purpose of getting more evidence of its mechanism, especially in regard to initiation and termination steps. Because of its low boiling point, liquid ammonia is not a convenient solvent for quantitative study of the reaction. Fortunately, the reaction also occurs in high yield in dimethyl sulfoxide (Me_2SO) solution.[13] We chose to study it in that solvent.

Experimental Section

Materials. All reagents and solvents were commercially available. Diethyl phosphonate (DEP) was vacuum distilled from calcium hydride. Me_2SO was freshly distilled under reduced pressure over CaH_2 before each experiment. Iodobenzene was also freshly redistilled before each experiment. Potassium *tert*-butoxide (*t*-BuOK) was freshly resublimed before each experiment.

Apparatus. Quantum yield measurements were carried out at 313 nm with a low pressure mercury lamp and a "merry-go-round". The whole apparatus was immersed in a water bath, the temperature of which ranged from 18 to 20 °C. For rate measurements and qualitative studies a Rayonet photochemical reactor equipped with 350-nm lamps was used. Quantitative measurements of iodide ion were performed by potentiometric titration with standard $AgNO_3$ solution. NMR spectra were recorded on a Jeolco Minimar 60-MHz nuclear magnetic resonance spectrometer.

Reaction of Diethyl Phosphite with *t*-BuOK. The reaction was followed by monitoring the NMR integral of the lower field portion of the P-bound proton doublet at various concentrations of *t*-BuOK with benzene being used as an internal standard. The integral decreased linearly as expected for complete reaction according to eq 5. The initial concentration of DEP was 1.16 M and the concentration of *t*-BuOK ranged from 0 to 0.9 M.

Spectrophotometric Studies. Materials were repurified as described above. KDEP solution was prepared by addition of the solvent (Me_2SO) to a weighed amount of *t*-BuOK followed immediately by the addition of an equivalent amount of DEP. In cases where *t*-BuOH-free KDEP was used, a roughly weighed sample of potassium metal was dissolved in liquid ammonia and titrated with DEP until the blue color disappeared. Most of the ammonia was evaporated under a stream of nitrogen, the required volume of Me_2SO was added, and the evaporation was continued under vacuum. The concentration of the KDEP solution was calculated on the basis of the weight of the DEP needed for the titration. Variations in the concentrations of the components were achieved by mixing stock solutions in appropriate amounts. Additives such as *t*-BuOH and 18-crown-6 ether were weighed directly into the final mixing vessel. Absorbance measurements were always carried out within a few minutes after completion of mixing.

The Effect of 18-Crown-6 on Light Absorption. Two Me_2SO solutions 0.157 M in iodobenzene and 0.033 M in KDEP, one without other constituents, the other containing also 0.04 M 18-crown-6 ether, were examined in 1-cm cells at 313 nm. They had absorbances of 1.60 and 1.75, respectively. Iodobenzene in Me_2SO at that concentration level, without KDEP, has absorbance 0.93.

In another experiment, three Me_2SO solutions 0.0765 M in iodobenzene and 0.0297 M in KDEP, one without other constituents, one containing also 0.032 M 18-crown-6 ether, the third containing 0.119 M 18-crown-6 ether, were similarly examined. Their absorbances were 0.66, 0.72, and 0.82, respectively. Iodobenzene (0.0765 M) in Me_2SO has absorbance 0.45.

Dependence of Velocity on Light Intensity. These experiments were conducted in a "merry-go-round" rotating within the Rayonet photochemical reactor which, when fully outfitted, contains 16 fluorescent lamps emitting maximally about 350 nm. In this apparatus, light intensity could be varied by varying the number of lamps. It was found that different groupings of four or five lamps gave essentially the same initial rate of iodide ion release, per lamp. It follows that the lamps were nearly alike in their output of light. Accordingly the number of lamps in the reactor is used as an index of light intensity and is symbolized *I*. In the three sets of runs performed, iodobenzene and KDEP concentrations were approximately 0.05 and 0.10 M, respectively. At these concentrations light absorption was incomplete but that is of no concern inasmuch as the fractional absorption was the same for all samples. Full data are presented in Table VII (see paragraph at end paper regarding supplementary material).

Quantum Yield Determination. *t*-BuOK was weighed into a three-necked flask to which Me_2SO was added followed immediately by a preweighed sample of DEP. The solution was stirred under dry nitrogen until all the *t*-BuOK dissolved and then iodobenzene was added. After about 5 min of stirring 3.0-mL aliquots were transferred to Pyrex test tubes which were flushed with dry nitrogen and immediately sealed with rubber stoppers. The test tubes were placed in the merry-go-round which was immersed in a water bath at 18.0–20 °C. At various times of radiation at 313 nm, the test tubes were removed, quenched by addition of ice water, and analyzed for iodide ion by potentiometric titration. Occasionally, samples were taken for GLC analysis for qualitative verification of the reaction. Often a duplicate was run simultaneously; the deviations between duplicate runs usually did not exceed 5%. A correction for dark reaction was made by determining the iodide contents of two unirradiated samples, one quenched at the beginning and the other at the end of the irradiation time, estimation of the iodide ion content for the relevant time by linear interpolation, and subtraction from the iodide ion content of the irradiated sample. The number of moles of photochemically released iodide ion divided by the total amount of light (in einsteins) absorbed by the solution during irradiation was taken as the quantum yield. Full data for one set of quantum yield determinations (set 56) are presented in Table I. Similar data for other sets appear in supplementary pages in the microfilm edition. The quantum yields presented in Table II are the average of results obtained at each concentration for different irradiation times.

Table I. Quantum Yields of the Reaction of Iodobenzene (0.144 M) with Varying Concentrations of KDEP at 313 nm (Experiment Set No. 56)

Run no.	[KDEP], M	Irradiation time, min[a,b]	Iodide released (mol × 10^5)	% reaction[c]	Φ
56d	0.397	0	0.58	1.36	
		5	1.43	3.34	50.2
		10	2.28	5.33	49.6
		10[d]	0.6	1.40	
56c	0.264	0	0.6	1.4	
		5	1.31	3.06	41.9
		10	2.01	4.7	41.6
		10[d]	0.6	1.4	
56b	0.176	0	0.48	1.12	
		5	1.06	2.48	33.7
		10	1.55	3.62	31.0
		10[d]	0.5	1.16	
56a	0.118	0	0.38	0.89	
		5	0.76	1.78	21.5
		10	1.1	2.57	20.4
		10[d]	0.41	0.96	

[a] Time zero is the beginning of irradiation; iodide ion formation at dark time "0 min" indicates reaction during mixing, dispensing of aliquots, etc. [b] Light flux 3.4 × 10^{-8} einstein/min. [c] Based on initial concentration of iodobenzene. [d] Unirradiated sample, quenched at t = 10 min.

Actinometry. The amount of light absorbed by the reaction mixtures in the quantum yield experiments was measured by the ferrioxalate method.[14] The measurements were performed in duplicate during the irradiation of the reaction mixtures and compared with an unirradiated sample. The values obtained for the flux that entered the test tubes were about 5 × 10^{-8} einstein/min.

Catalysis by Phenylazotriphenylmethane (PAT). A solution 0.053 M in iodobenzene and 0.103 M in KDEP kept without illumination at 61–62 °C for 120 min released only 2.53% of iodide ion. A solution containing also 5.55 mole % of PAT similarly treated released 13.7% of iodide ion (based on iodobenzene).

Reaction in the Presence of Azobisisobutyronitrile (AIBN). Reactant concentrations were similar to those in the above experiment. A reaction mixture containing also 5.7 mole % of AIBN during 25 min at 82 °C without illumination released less (77% as much) iodide ion than was formed under the same conditions in the absence of AIBN.

Inhibition by Di-*tert*-butyl Nitroxide. Irradiation of a reaction mixture 0.112 M in KDEP and 0.074 M in iodobenzene at 350 nm in the presence of 4.4 mole % of di-*tert*-butyl nitroxide was found to give 1.49, 3.23, 5.98, 13.7, and 25.5% of iodide ion, respectively, at 0, 2,

Table II. Summary of Quantum Yield Experiments

Run no.	[PhI], M	[KDEP],[a] M	[DEP], M	[*t*-BuOK], M	Φ	f_{PhI}[b]	Φ/f_{PhI}
40a	0.059	0.117		0.002	21.0[c]	0.34[c]	62
b	0.118	0.233		0.004	35.4	0.27	132
c	0.236	0.466		0.009	44.1	0.21	214
41a	0.124	0.245		0.009	13.4	0.26	51
b	0.248	0.245		0.009	13.5	0.26	52
c	0.495	0.245		0.009	8.8	0.26	34
42a	0.123	0.245		0.009	15.2	0.26	58
b	0.37	0.245		0.009	15.5	0.26	59
c	0.37	0.245		0.009	15.8	0.26	60
64a	0.122	0.223			39.7	0.27	145
b	0.254	0.223			43.1	0.27	158
c	0.496	0.223			41.3	0.27	151
47a	0.145	0.275		0.024	59.5	0.25	235
b	0.145	0.299	0.252		16.6	0.24	68
c	0.145	0.299	0.711		17.3	0.24	71
45a	0.158	0.321		0.003	23.0	0.24	96
b	0.158	0.324	0.316		14.4	0.24	60
49a	0.152	0.327		0.003	17.1	0.24	72
b	0.152	0.330	0.314		10.4	0.24	44
46a	0.115	0.114	0.345		6.9[d]	0.34	20
b	0.115	0.237	0.222		17.8	0.27	66
c	0.115	0.459		0.006	20.5	0.21	99
48a	0.153	0.150	0.158		10.3	0.32	33
b	0.153	0.300	0.008		16.7	0.24	68
50a	0.142	0.115			8.6	0.35	25
b	0.142	0.230			13.3	0.275	48
c	0.142	0.460			21.1	0.21	103
51a	0.143	0.114			9.5	0.34	28
b	0.143	0.228			20.0	0.27	74
c	0.143	0.457			28.0	0.21	133
52a	0.145	0.116			6.1	0.34	18
b	0.145	0.350			15.9	0.23	70
c	0.145	1.04			32.0	0.15	213
54a	0.139	0.115			6.8	0.35	19
b	0.139	0.231			13.8	0.27	51
c	0.139	0.463			22.1	0.21	104
55a	0.143	0.175			9.7	0.30	32
b	0.143	0.264			13.5	0.26	52
c	0.143	0.394			17.2	0.22	78
d	0.143	0.591			24.2	0.188	129
56a	0.144	0.118			21.0	0.344	61
b	0.144	0.176			32.4	0.300	108
c	0.144	0.264			41.8	0.250	167
d	0.144	0.397			49.9	0.216	231
57a	0.143	0.176			9.7	0.35	28
b	0.143	0.264			13.8	0.30	46
c	0.143	0.396			19.5	0.236	83
d	0.143	0.593			24.6	0.198	124
65a	0.401[e]	0.792			(5.6)[f]		
b	1.39[e]	0.676			(8.2)[g]		

[a] Prepared by mixing DEP and *t*-BuOK in Me_2SO, with complete conversion to KDEP assumed. [b] f_{PhI} is the fraction of the incident light absorbed by iodobenzene. [c] Absorbance of solution ca. 0.974; no correction made for light not absorbed. [d] Absorbance of solution ca. 1.90; no correction made for light not absorbed. [e] Bromobenzene. [f] Absorbance of solution 0.33, but no correction applied. [g] Absorbance of solution 0.97, but no correction applied.

5, 10, and 20 min, while in the absence of DTBN an otherwise identical mixture gave 1.21, 8.08, 17.6, 28.9, and 68.9% reaction, respectively, for the same irradiation times.

Inhibition by $CuCl_2$, $CuSO_4$, O_2, and $FeCl_3$. Solutions 0.102 M in KDEP and 0.057 M in iodobenzene were irradiated for 5, 10, and 15 min at 350 nm. Results obtained for solutions containing also 0.61 mole % $CuCl_2$, 1.27 mole % $CuSO_4$, and O_2 were within ±3.5% of the "uninhibited" reaction over this range (90% reaction was obtained at 15 min). $FeCl_3$ (3.9 mole %) inhibited the reaction so that after 5 min (about one half-life of the uninhibited reaction) only 5% of iodide was released.

Supplementary Data. In Tables III–IX, which appear in supplementary pages in the microfilm edition of this journal, are listed detailed data on spectrophotometric experiments, on the dependence of rate on light intensity, on quantum yield determinations, and on correlation of f_{CT}/Φ with $1/[\mathrm{KDEP}]$.

Results

Description. In the course of their exploration of several solvents for reaction 1, Bunnett, Scamehorn, and Traber[13] exposed a solution of iodobenzene and a twofold excess of potassium diethyl phosphite (KDEP) in Me_2SO, contained in a Pyrex flask, to irradiation for 4 h with "350-nm" lamps. They observed quantitative release of iodide ion and isolated a 68% yield of diethyl phenylphosphonate. (The shortfall from 100% was attributed to losses during isolation.) GLC tracings for

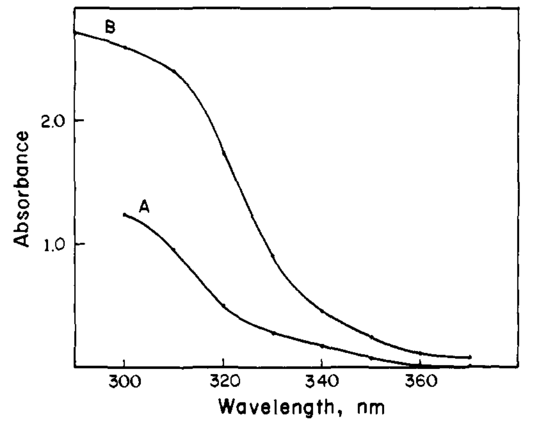
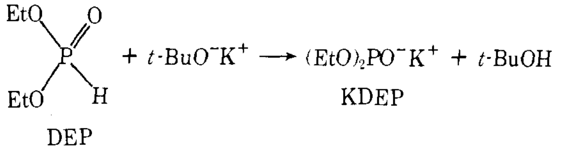


Figure 1. Spectra of (A) 0.149 M iodobenzene in Me_2SO and (B) 0.149 M iodobenzene + 0.302 M KDEP in Me_2SO. Measurements in 1-cm cells.

products formed in Me_2SO indicate diethyl phenylphosphonate to be the sole product formed.

Reaction of Diethyl Phosphonate (DEP) with Potassium *tert*-Butoxide (*t*-BuOK). By observation of the intensity of the lower field absorption of the ^1H NMR doublet due to the P-bound proton of DEP, in a series of solutions containing varying proportions of DEP and *t*-BuOK, we observed that the reaction of DEP with *t*-BuOK in Me_2SO forms KDEP and *t*-BuOH quantitatively, according to eq 5.



(5)

Catalysis and Inhibition. The thermal reaction of KDEP with iodobenzene, without irradiation, is very slow. A typical reaction solution formed only 2.5% of iodide ion during 2 h at 61–62 °C.

Phenylazotriphenylmethane (PAT) stimulates release of iodide ion. Under the conditions mentioned, a reaction solution containing also 5.55 mole % of PAT released 13.7% of iodide ion, or about two iodide ions per molecule of PAT originally present. However, similar experiments involving azobisisobutyronitrile at 81–84 °C gave no indication of catalysis by this radical source.

Di-*tert*-butyl nitroxide at the level of 4.4 mole % was shown to inhibit the photostimulated reaction of KDEP with iodobenzene, reducing the rate to as little as a third of that without the nitroxide. This nitroxide was demonstrated not to affect the absorbance of light at 313 or 350 nm by solutions of KDEP and iodobenzene. Therefore its inhibiting effect is not to be attributed to competitive absorption of photons.

Neither the addition of $CuCl_2$ (0.6 mole %) nor $CuSO_4$ (1.3 mole %) nor exposure of the reacting solution to dioxygen (O_2) caused any diminution of the rate of the photostimulated reaction. The addition of $FeCl_3$ (3.9 mole %) sharply reduced the rate of the photostimulated reaction, but the reduction is perhaps caused by competing absorption of light, for reaction solutions to which $FeCl_3$ has been added show greatly enhanced absorbance at 313 and 350 nm.

Potassium iodide (9 mole % in respect to iodobenzene) was shown to have no effect on reaction rate.

Spectrophotometric Studies. KDEP is transparent in Me_2SO in the region 300–370 nm. Iodobenzene absorbs weakly, as shown in Figure 1; the molar extinction coefficient diminishes from 8.3 at 300 nm to 0.051 at 370 nm. However, mixtures of KDEP and iodobenzene absorb more strongly, as shown also in Figure 1. The reaction product, diethyl phenylphosphonate, absorbs very weakly; its extinction coefficient is about one-tenth that of iodobenzene through most of this range. There is enhanced absorption also in solutions of KDEP and diethyl phenylphosphonate, but the absorbance is less than in solutions of KDEP and iodobenzene at the same levels of concentration.

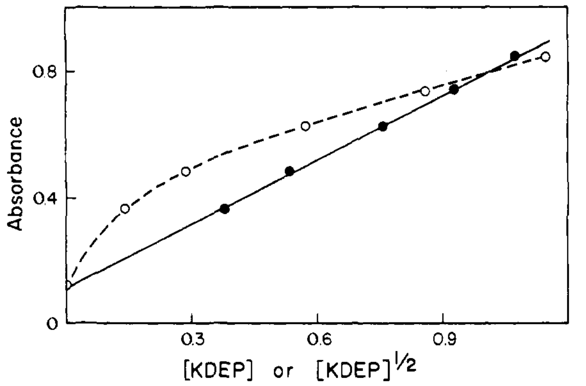


Figure 2. Absorbance at 313 nm of solutions of constant iodobenzene concentration (0.02 M) and varying KDEP concentration, in 1-cm cells in Me_2SO: open circles, as function of [KDEP]; filled circles, as function of $[KDEP]^{1/2}$. The intercept of the linear regression line which has been drawn based on the latter points is 0.109, and the absorbance of 0.149 M PhI without KDEP is 0.122.

The increase of absorbance on mixing KDEP with iodobenzene or diethyl phenylphosphonate is attributed to charge-transfer complex formation between diethyl phosphite ion and the aromatic compound.

Figure 2 displays the absorbance at 313 nm of mixtures of varying concentrations of KDEP with 0.02 M iodobenzene. There is a curvilinear dependence of absorbance on KDEP concentration. However, absorbance is linearly related to the square root of KDEP concentration, as represented in Figure 2, and the intercept is the absorbance expected for iodobenzene in that concentration.

When the KDEP concentration was held constant, though in excess, and iodobenzene concentration was varied, the measured absorbance was linear with iodobenzene concentration with intercept zero (plot not shown). Addition of *t*-BuOH to a solution of KDEP and iodobenzene in Me_2SO, previously free of *t*-BuOH, had negligible effect on the absorbance. However, addition of 18-crown-6 ether[15] to a solution of KDEP, obtained via reaction 5, and iodobenzene in Me_2SO caused a substantial increase in absorbance, and a higher concentration of 18-crown-6 caused a greater increase. This crown ether has no absorption at the wavelength (313 nm) of the measurements.

The square root dependence evident in Figure 2 is attributed to ion pairing by KDEP. If only free diethyl phosphite ion can form a charge transfer complex with iodobenzene, but ion-paired diethyl phosphite ion cannot, and if the ion pairing association constant is high, observable behavior should match that seen. For *t*-BuOK, the ion pairing association constant is 270 M^{-1} in Me_2SO.[16] If the constant is of similar magnitude for KDEP, which is conceivable, KDEP is only about 11% dissociated at the lowest concentration for which there is a datum in Figure 2, and even less at higher concentrations.

We considered another model whereby to interpret the curvature in the plot of absorbance vs. KDEP concentration (Figure 2), namely, that the equilibrium between iodobenzene and diethyl phosphite ion on the one hand and charge-transfer complex on the other lay so far toward the complex at higher KDEP concentrations that absorbance leveled off as the plateau for full conversion of iodobenzene to the complex was approached. A modified Benesi-Hildebrand treatment[17] was applied, but it failed to give an internally consistent interpre-

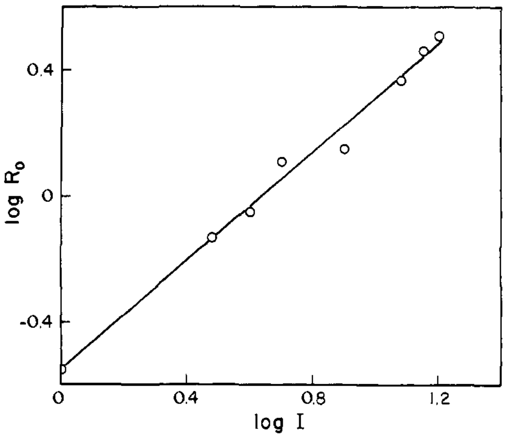


Figure 3. Logarithm of initial rate (R_0) of reaction of iodobenzene with KDEP in Me_2SO vs. logarithm of light intensity.

tation of our observations. This model was therefore discarded.

Dependence of Velocity on Light Intensity. We found reaction rate and the closely related quantum yield to be sensitive to impurities in the reagents or solvent. In early experiments the reproducibility between runs was not very good, but it was much improved when freshly resublimed *t*-BuOK and freshly redistilled Me_2SO were employed. Even so, it was less than fully satisfactory. On the other hand, reproducibility was good within any set of runs based on the same batches of *t*-BuOK and Me_2SO.

In three sets of runs the dependence of the initial rate on light intensity was studied. Data for the most extensive set, comprising eight runs, are plotted logarithmically in Figure 3; the logarithm of initial rate is plotted against the logarithm of an index of the light intensity (see Experimental Section). Despite some scatter, the points define a line of slope 0.86 ± 0.04. Plots of the same type for the less extensive sets of runs had slopes of 0.78 ± 0.04 and 0.88 ± 0.11, and the weighted average of the three is 0.84. The dependence of initial rate on light intensity is somewhat less than first-power but much closer to it than to the half-power which prevails for many photocatalyzed radical reactions.[18b]

Quantum Yield Experiments. These were conducted in Pyrex test tubes in a "merry-go-round" apparatus with exposure to monochromatic light at 313 nm and with ferrioxalate actinometry. The dependence of quantum yield on the concentrations of iodobenzene, KDEP, and/or excess DEP was investigated. Study of its dependence on excess *t*-BuOK was frustrated by the release of large amounts of iodide ion in the dark. The concentrations of reagents used were high enough to give absorbances in excess of 2.0, and thus virtually complete absorption of photons. (Exceptions were runs 40a and 46a for which absorbances at 313 nm in 1-cm cells were approximately 0.97 and 1.90, respectively.) Results are summarized in Table II.

In Table II, each set of runs (e.g., 40a, 40b, and 40c) is based on the same batches of resublimed *t*-BuOK and redistilled Me_2SO, but different sets are in general based on different batches. Because of the apparent sensitivity of reaction rate to impurities that vary somewhat from batch to batch, comparisons should be made principally within the runs of a set.

All the raw quantum yields measured greatly exceed unity.

In set 40, the concentrations of both iodobenzene and KDEP vary in parallel, and the amount of excess *t*-BuOK is too small to be troublesome. The overall quantum yield, Φ, increases steadily with increasing concentration.

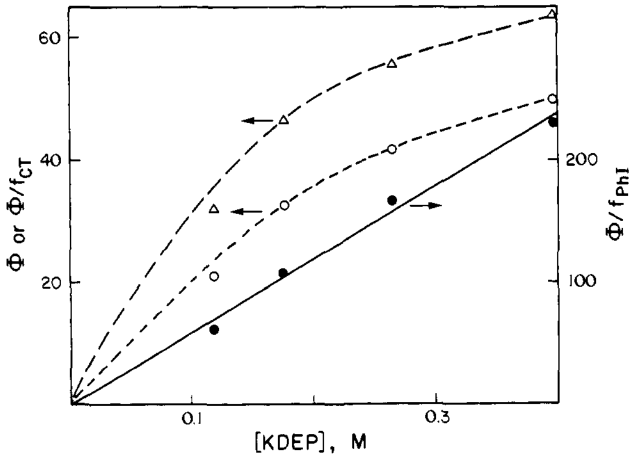


Figure 4. Quantum yield at 313 nm as function of KDEP concentration: open circles, Φ, the raw quantum yield (left scale); triangles, Φ/f_{CT}, where f_{CT} is the fraction of light absorbed by the charge transfer complex (left scale); filled circles, Φ/f_{PhI}, where f_{PhI} is the fraction of light absorbed by iodobenzene (right scale); the straight line is by linear regression analysis based on the four data points without imposed condition to pass through the origin.

In sets 41, 42, and 64, KDEP concentration is held constant and iodobenzene concentration is varied. Within set 42 or 64, the quantum yield is substantially constant as iodobenzene concentration is varied as much as fourfold. The remarkable difference in quantum yield between these two ostensibly similar sets testifies, we think, to the presence of unknown impurities in the reagents used for one set more than in the reagents used for the other. Within set 41, the quantum yield in run 41c is exceptional, enough so to warrant its rejection from the data.

In sets 47, 45, and 49, the concentrations of iodobenzene and KDEP are kept constant but DEP in varying amounts is sometimes present. The presence of excess DEP causes a decrease in quantum yield, but the effect impresses us for its moderation.

In sets 46 and 48, two variables, KDEP and DEP concentrations, are changed jointly but with the sum of the two constant. The quantum yield increases as KDEP concentration waxes and DEP concentration wanes.

In sets 50-52 and 54-57, inclusive, iodobenzene concentration is maintained constant and KDEP concentration is varied. In all sets Φ rises with increasing KDEP concentration.

Quantum Yields and Light Absorption. Spectrophotometric studies (above) show that, of the light absorbed by solutions containing iodobenzene and KDEP, part is absorbed by iodobenzene and part by its charge-transfer complex with diethyl phosphite ion. We now ask: which part stimulates the substitution reaction of eq 1?

Inasmuch as iodobenzene undergoes negligible photolysis under the conditions of the quantum yield determinations, Φ should be zero at zero concentration of KDEP. For each of data sets 50-52 and 54-57, a plot of Φ against KDEP concentration was constructed; five of the plots were nonlinear, as for example that in Figure 4 for set 56, and the two that were approximately linear had intercepts far from zero.

Either by direct measurement or by reckoning from valid relationships derived from other measurements, one can apportion the total absorbance into parts attributed to iodobenzene and to its charge-transfer complex with diethyl phosphite ion. The latter method involves an assumption, justification for which is presented above, that only a tiny fraction of the iodobenzene is converted to the charge-transfer complex.

Let us consider the possibility that reaction is provoked by the absorption of photons by the charge-transfer complex. In that case it would be the fraction of the incident light absorbed by the complex that were responsible for reaction. The fraction absorbed by iodobenzene would be wasted insofar as the substitution reaction were concerned, and a correction could be applied to the measured quantum yield. The correction would involve dividing Φ by f_{CT}, the fraction of the light absorbed by the complex.

Corrected quantum yields thus reckoned were plotted against KDEP concentration. The resulting plots were also curved; see Figure 4, for instance. Conceivably the curvature was consistent with a relationship of the mathematical form of eq 6. A test of that possibility is suggested by eq 7, which is

$$\frac{\Phi}{f_{\mathrm{CT}}} = \frac{p[\mathrm{KDEP}]}{q + [\mathrm{KDEP}]} \tag{6}$$

$$\frac{f_{\mathrm{CT}}}{\Phi} = \frac{q}{p[\mathrm{KDEP}]} + \frac{1}{p} \tag{7}$$

the invert of eq 6. Plots of f_{CT}/Φ vs. $1/[\mathrm{KDEP}]$ should be linear, with slope q/p and intercept $1/p$. In fact, such plots were linear for experiment sets 50–52 and 54–57. The results of linear regression analysis are tabulated in Table IX (in the supplementary material). The correlation coefficients for the seven sets are 0.987 or higher, and for three sets they are 0.999 or higher. Inasmuch as obedience to the mathematical form of eq 6 can be given a reasonable chemical interpretation (vide infra), it seems possible that the light absorbed by the charge-transfer complex is the light that actually stimulates reaction.

Now let us consider the possibility that the photons captured by iodobenzene are the ones that stimulate the substitution reaction. If so, the measured quantum yield should be corrected by dividing it by the fraction of the light absorbed by iodobenzene, which we symbolize f_{PhI}. Our evaluations of f_{PhI} and of Φ/f_{PhI} are listed in Table II. Φ/f_{PhI}, the corrected quantum yield, is found to be related to [KDEP] in an approximately linear fashion, with intercept zero within experimental error, for the seven sets of runs (50–52 and 54–57) suitable for such analysis. For example, see Figure 4. Plots of log (Φ/f_{PhI}) vs. log [KDEP] have slopes between 1.02 and 1.27 for these data sets and the weighted average slope is 1.12.

As discussed below, the linear dependence of Φ/f_{PhI} can also be given a reasonable chemical interpretation. In terms of it, the corrected quantum yield depends on a power of KDEP concentration somewhat greater than unity. In their studies of the photochemical exchange of iodine between iodobenzene and radio-labeled I_2, Levy, Meyerstein, and Ottolenghi[12] found that it was the light absorbed by iodobenzene that brought about reaction rather than that absorbed by its charge-transfer complex with I_2.

Experiments with Bromobenzene. In descriptive studies it became evident that bromobenzene is much less reactive than iodobenzene with KDEP. In two runs (65a and 65b, Table II) the amount of bromide ion produced was measured as a function of radiation dosage at 313 nm. Because bromobenzene and its presumed charge-transfer complex with diethyl phosphite ion absorb less strongly than for iodobenzene, it was necessary to use higher reactant concentrations than in the runs with iodobenzene. Nevertheless, light absorption was incomplete. In a rectangular cell with 1-cm light path, only 53% of the incident 313-nm radiation was absorbed by the solution used in run 65a and only 89% by that used in run 65b. The apparent quantum yields under these conditions were 5.6 and 8.2, respectively.

Discussion

Salient results from this study are that in all cases the raw quantum yield for reaction 1 exceeds unity, that it is independent of iodobenzene concentration, and that reaction rate depends on a power of the light intensity slightly less than one. Some of the light is absorbed by the iodobenzene and some by its charge-transfer complex with diethyl phosphite ion and, on the basis of a different mathematical model for each, either part can rationally be interpreted to be the light that effectively stimulates the reaction.

The fact that the raw quantum yield exceeds unity, being frequently between 20 and 50 (see Table II), indicates a chain mechanism with initiation by the action of photons and propagation in steps that do not require light. The facts that the reaction is catalyzed by thermal decomposition of phenylazotriphenylmethane (PAT) and inhibited by di-*tert*-butyl nitroxide indicate a radical chain mechanism. PAT is a source of phenyl radicals[20] and di-*tert*-butyl nitroxide a scavenger of highly reactive radicals.[21]

The fact that the reaction rate is proportional approximately to the 0.84 power of light intensity shows that the predominant termination steps are *unimolecular* in a radical or radicals that participate in the propagation cycle. If termination were strictly unimolecular in propagating radical, dependence purely on the first power of light intensity would be observed. If it were bimolecular in propagating radicals, the rate would be proportional to the square root of light intensity.[22] The observed dependence is closer to first power than to one-half power.

Termination steps unimolecular in propagating radicals are unusual, though they have been encountered before.[23] An obvious case would be reaction of a propagating radical with a rather unreactive radical species that happens to be present in the system, to form nonradical products. Of greater present interest is reaction of a reactive, propagating radical with a nonradical species to form a lethargic radical (and perhaps some nonradical by-product) that is incapable of carrying on the main propagating sequence or of engaging in activities that would lead back into the main propagating sequence. The lethargic radicals tend to accumulate and to react with each other or to capture reactive, propagating radicals, either way to form nonradical products. If the latter, the consequence of the formation of one lethargic radical is to terminate two propagating chains. In either case, the effective termination step is that in which the lethargic radical is generated.

Bartlett and Altschul[23] found the polymerization of allyl acetate to be first order in the benzoyl peroxide catalyst employed, and attributed the kinetic behavior to termination steps in which the growing polymer radical abstracted hydrogen from allyl acetate to form a nonradical polymer molecule and an allylic radical highly stabilized by resonance. That historically important example is a fine illustration of the principle.

The overall rate law for a radical chain reaction is composite, being determined by the rate laws that govern initiation, termination, and the propagation steps that are kinetically crucial by virtue of the termination steps that prevail.[18a,24] Judgments concerning the ambiguous question of which part of the light actually brings about reaction, about the dependence of quantum yield on about the 1.12 power of KDEP concentration if the light absorbed by iodobenzene is the effective light, and about the independence of quantum yield from iodobenzene concentration must therefore await consideration of the probable character of the initiation and termination steps. We do note, however, that the concentration of iodobenzene in our experiments was high enough to ensure the capture of virtually every incident photon; in consequence, iodobenzene is not expected to appear in the overall rate law insofar as initiation is concerned.

The Photolysis of Iodobenzene. Iodobenzene has significant UV absorption at wavelengths as high as 370 nm.[12a,25] In the gas phase the excited species fragments after a lifetime of only about a picosecond.[26] In hydrocarbon solvents, however, photolysis appears to generate a species of longer lifetime that is capable of reverting to ground state iodobenzene.

Evidence for the latter concept comes mainly from studies of the effect of dioxygen or nitric oxide (NO) on the quantum yield when photolysis is conducted in solvents such as methylcyclohexane.[12,27-30] The quantum yield is exceedingly low in the absence of O_2 or NO but rises steeply as either is introduced, ultimately approaching unity.[27-30]

It has been suggested that in solution the phenyl radical and iodine atom that result from fragmentation are generated as a solvent-caged radical pair,[12] symbolized $(\mathrm{Ph{\cdot}{\cdot}I})$. The caged radical pair is postulated to revert rapidly to iodobenzene unless intercepted by some external reagent such as NO or O_2. Diiodine (I_2), benzene, and toluene may also function as interceptors.[12]

Insofar as interception by dioxygen is concerned, this proposal imputes to phenyl radical in the caged pair a selectivity for reaction with O_2 as compared to methylcyclohexane much greater than indicated for the free phenyl radical by the measurements of Russell and Bridger.[20,31] Thus O_2 at the level of 10^{-4} M is effective, implying that it is more reactive than the solvent (7.8 M) or that $k(\mathrm{O_2})/k(\mathrm{CH_3C_6H_{11}}) > 7.8 \times 10^4$ whereas this rate constant ratio from Russell and Bridger is only 7.7×10^2. There is a discrepancy of at least two orders of magnitude. Perhaps the species that is so selective has some other structure than the caged radical pair. Maybe it is π-iodobenzene analogous to the π-chlorobenzene indicated by the work of Fox, Nichols, and Lemal.[32]

Whatever the proper interpretation, the important feature for our present purposes is that in solution some type of activated iodobenzene is generated that reverts to ground state iodobenzene unless intercepted by an external reagent.

Initiation. Let us first consider the possibility that the light absorbed by the iodobenzene is that which initiates reaction. The model of eq 8 and 9 merits our attention.

$$\mathrm{PhI} \underset{k_{-i}}{\overset{h\nu}{\rightleftarrows}} (\mathrm{PhI})^* \qquad (8)$$

$$(\mathrm{PhI})^* + (\mathrm{EtO})_2\mathrm{PO}^- \xrightarrow{k_9} [\mathrm{PhPO(OEt)_2}]^-\cdot + \mathrm{I}\cdot \qquad (9)$$

The species symbolized (PhI)* may be the caged radical pair, on π-iodobenzene, or it may have some other structure. Step 8, reverse, represents its reversion to ground state iodobenzene and step 9 its reaction with diethyl phosphite ion acting as an interceptor analogous to O_2, NO, or I_2. If the reversion step is much faster than step 9 even at the highest concentrations of KDEP employed, the rate of initiation should be linearly dependent on diethyl phosphite ion concentration or, if ion-paired KDEP is highly reactive with (PhI)*, on KDEP concentration. The radical anion formed in step 9 would enter the propagation cycle at step 4.

An alternative model suggested by the work of Ruzo, Bunce, and Safe[33] comprises steps 8 and 10. In step 10 the activated iodobenzene species generated in step 8 accepts an electron from the diethyl phosphite ion, forming phenyl radical, iodide ion, and diethoxyphosphinyl radical. The phenyl radical may enter the propagation cycle at step 3.

$$(\mathrm{PhI})^* + (\mathrm{EtO})_2\mathrm{PO}^- \xrightarrow{k_{10}} \mathrm{Ph}\cdot + \mathrm{I}^- + (\mathrm{EtO})_2\mathrm{PO}\cdot \qquad (10)$$

Both of these initiation models, that comprising steps 8 and 9 and that consisting of steps 8 and 10, call for linear dependence of initiation rate on nucleophile concentration.

We can conceive of initiation models which would call for initiation to be zero order in nucleophile. We mention them despite their being inconsistent with the prior work cited. One is the primitive model in which photolysis of iodobenzene gives directly phenyl radicals which enter the propagation cycle at step 3. Nearly the same would be a model comprising steps 8 and 9 but with step 9 much faster than step 8, reverse. Another would be one consisting of steps 8 and 10 with step 10 much faster than step 8, reverse. As we show below, our observed rate law would require any such unlikely initiation mechanism to be coupled with an improbable termination step.

Now let us consider the possibility that the light absorbed by the charge-transfer complex (CT) is that which provokes reaction, with attention specifically to the initiation model of Scheme II.

Scheme II

$$\mathrm{PhI} + (\mathrm{EtO})_2\mathrm{PO}^- \rightleftarrows \underset{\mathrm{CT}}{\mathrm{PhI{\cdot}(EtO)_2PO^-}} \qquad (11)$$

$$\mathrm{CT} \underset{k_{-j}}{\overset{h\nu}{\rightleftarrows}} \underset{\mathrm{M}}{\overline{\mathrm{Ph}\cdot\ \mathrm{I}^-\ \cdot\mathrm{OP(OEt)_2}}} \qquad (12)$$

$$\mathrm{M} \xrightarrow{k_{13}} \mathrm{PhPO(OEt)_2} + \mathrm{I}^- \qquad (13)$$

$$\mathrm{M} + \mathrm{KDEP} \xrightarrow{k_{14}} [\mathrm{PhPO(OEt)_2}]^-\cdot + \mathrm{KI} + (\mathrm{EtO})_2\mathrm{PO}\cdot \qquad (14)$$

In this model, an equilibrium reaction to form CT (eq 11) is followed by absorption of a photon which fractures CT to form a solvent-caged melange (M) of a phenyl radical, an iodide ion, and a diethoxyphosphinyl radical. Though reversion of m to CT seems unlikely, it is included as a formal possibility. A more probable unproductive step is reaction 13, in which the two radicals of M colligate and extrude iodide ion. Although that step yields diethyl phenylphosphonate, the main product of the overall reaction, it is unproductive for the initiation of radical chains, and the raw quantum yields far in excess of unity show that most of the overall reaction must occur in chain fashion. However, step 14, in which the phenyl radical of M is attacked by diethyl phosphite ion, forms the radical anion $[\mathrm{PhPO(OEt)_2}]^-\cdot$ which can enter the propagation cycle (Scheme I) at step 4. The diethoxyphosphinyl radical byproduct of step 14 is considered in this model to be ineffective either for entry into the propagation cycle or for termination.

From Scheme II, on the basis of the steady-state assumption, one derives that the rate of initiation via production of $[\mathrm{PhPO(OEt)_2}]^-\cdot$ is given by

$$R_\mathrm{i} = \frac{k_{14} I g' f_\mathrm{CT}[\mathrm{KDEP}]}{k_{-\mathrm{j}} + k_{13} + k_{14}[\mathrm{KDEP}]} \qquad (15)$$

where g' is the fraction of the photons absorbed by CT that form M. The right-hand side of eq 15 has the same mathematical form as the right side of eq 6. The fact that f_CT/Φ correlates linearly with 1/[KDEP] (vide supra) requires that this model for initiation be considered seriously.

In connection with the initiation model of Scheme II, one must consider the possibility that the constituents of melange M may diffuse apart and that the phenyl radical may then start propagation, entering the cycle at step 3. If so, one would have to invoke colligation of separated phenyl and diethoxyphosphinyl radicals as an effective competitor with step 3 in order to account for the mathematical form of eq 6. But that would constitute a termination step incompatible with the experimental finding that rate is proportional nearly to the first power of light intensity. Therefore initiation via phenyl radicals from diffusive separation of melange M must be so infrequent as to have no discernible consequence, or the model of Scheme II must be rejected.

It is evident from this discussion that plausible initiation mechanisms can be formulated to account for initiation either by the iodobenzene-absorbed photons or by the CT-absorbed photons.

Termination. Two attractive termination steps, both unimolecular in a reactive, propagating radical, are represented in the equations:

$$[\mathrm{PhI}]^{-}\cdot \xrightarrow{k_{16}} \mathrm{Ph}^{-}: + \mathrm{I}\cdot \tag{16}$$

$$\mathrm{Ph}\cdot + (\mathrm{EtO})_2\mathrm{PO}^{-} \xrightarrow{k_{17}} \mathrm{Ph}^{-}: + (\mathrm{EtO})_2\mathrm{PO}\cdot \tag{17}$$

The first is abnormal scission of the iodobenzene radical anion to form phenyl anion and iodine atom. Although available evidence indicates the opposite mode of scission (eq 2) in the case of iodobenzene radical anion, scission in the sense of eq 16 has been observed for other radical anions, for example, that of triphenylstibine. A study by Rossi and Bunnett[34] showed that the sense of rupture of several radical anions of type $[\mathrm{C_6H_5X}]^{-}\cdot$ tends to correlate with the electronegativities of the elements X vs. carbon. The "extra" electron tends to go with whichever fragment has the first atom of higher electronegativity, that is, to give phenyl radical and X anion when X is more electronegative, or phenyl anion and X radical when carbon is more electronegative. The borderline between the two modes of scission is not precisely defined. Diphenylselenide radical anion appears to rupture in part each way. Consultation of electronegativity values (C, 2.5; Se, 2.4; I, 2.5)[35] suggests the possibility that a small fraction of iodobenzene radical anion may rupture in the sense of eq 16. The iodine atom produced in step 16 would be a rather unreactive radical, incapable of leading back into the main propagation sequence. The phenyl anion would merely take a proton (e.g., from *t*-BuOH) and form benzene.

Reaction 17 is also a reasonable possibility for termination unimolecular in propagating radical. Other work[5,36] has provided evidence that electron transfer from nucleophile to aryl radical may accompany or even eclipse combination of the radical with the nucleophile to establish a covalent bond. In the interaction of diethyl phosphite ion with *o*-halophenyl radicals, electron transfer is a major pathway.[36] The diethoxyphosphinyl radicals produced in reaction 17 would be quite reactive,[37a] but, so long as their reactions did not lead back into the propagation cycle of Scheme I, reaction 17 would qualify as a termination step.

As discussed below, if either reaction 16 or 17 were the termination step, there could be no net contribution of KDEP concentration of the rate law from propagation and termination. If initiation is due to the iodobenzene-absorbed photons and were zero order in KDEP, for example, because step 9 or 10 were much faster than the reverse of step 8, termination unimolecular in phenyl radical would need to be considered.

Inasmuch as a truly unimolecular decomposition of phenyl radical is preposterous, and if the introduction of additional concentration factors into the rate law is to be avoided, such a termination step would have to involve reaction with some species present in constant amount within any set of runs. Dimethyl sulfoxide, the solvent, comes to mind, but its reaction with phenyl radical (to relinquish a hydrogen atom) is exceedingly slow,[20] probably too slow to account for termination in this system. Also, it is unclear what the $\mathrm{CH_3SOCH_2}\cdot$ radical would do. Alternatively, one might invoke reaction of phenyl radical with some unidentified adventitious impurity. Though that would not be intellectually satisfying, we must acknowledge that adventitious impurities play some role because there was significant variation in measured quantum yields from ostensibly identical reaction solutions made up from different batches of *t*-BuOK and $\mathrm{Me_2SO}$.

Though we can identify no conceivable step as a good candidate for "unimolecular" termination involving phenyl radical, we cannot totally exclude some such process as a possibility. However, as shown below, such an improbable termination step would require an unlikely initiation step in order to conform to the overall rate law.

Of the three termination mechanisms we have considered, none accounts for the fact that reaction rate depends on a power of light intensity somewhat less than one (0.84) or (if the iodobenzene-absorbed photons are those that provoke reaction) that the quantum yield depends on a power of KDEP concentration somewhat greater than one (1.12). It is therefore necessary to consider a termination mechanism bimolecular in propagating radical, such as the colligation of two phenyl radicals:

$$\mathrm{Ph}\cdot + \mathrm{Ph}\cdot \rightarrow \mathrm{Ph{-}Ph} \tag{18}$$

Although no biphenyl has been detected as a by-product, this is a familiar type of termination step. To the extent that it operated in competition with a termination step unimolecular in propagating radical, it would tend to reduce the order in light intensity below unity (to a limit of 0.5; vide supra) and to raise the order in KDEP above unity (to a limit of 1.5; see below).

Rate Laws. We have considered three conceivable patterns for the dependence of initiation rate on KDEP concentration: linear dependence, curvilinear dependence, and independence. Each possibility must be taken into account in formulating rate laws.

If reaction is provoked by the iodobenzene-absorbed photons, the kinetic consequences of initiation via steps 8 and 9 or via steps 8 and 10 are the same. We shall for derivation purposes represent the forward rate of step 8 as gI, where I is the light intensity and g the fractional efficiency in forming the relevant product. Also we will represent the rate coefficient for step 8, reverse, as $k_{-\mathrm{i}}$, and the rate coefficient for step 9 or 10 as k_{a}. If the reverse of step 8 is much faster than step 9 or 10, the rate of initiation is given by

$$R_{\mathrm{i}} = (Igf_{\mathrm{PhI}}/k_{-\mathrm{i}})k_{\mathrm{a}}[\mathrm{Nu}] \tag{19}$$

where Nu represents diethyl phosphite ion or ion-paired KDEP.

If reaction is provoked by the CT-absorbed photons, the kinetic consequence of initiation according to Scheme II should be curvilinear response, as expressed in eq 15, above.

If the iodobenzene-absorbed photons actually stimulate the reaction, and step 9 or 10 is much faster than the reverse of step 8, eq 20 obtains.

$$R_{\mathrm{i}} = Igf_{\mathrm{PhI}} \tag{20}$$

By means of the usual steady state derivations,[18a,24] one obtains eq 21, in which x is the concentration of either product of eq 1, as the rate law if initiation is governed by eq 19, propagation occurs as in Scheme I, and termination occurs via step 16. This calls for reaction first order in nucleophile and in light intensity and zero order in iodobenzene, approximately as observed.

$$\mathrm{d}x/\mathrm{d}t = k_3k_aIgf_{\mathrm{PhI}}[\mathrm{Nu}]/k_{17}k_{-\mathrm{i}} \tag{21}$$

Likewise, if initiation is governed by eq 19 and termination occurs via step 17, the rate law derived is that of eq 22.

$$\mathrm{d}x/\mathrm{d}t = k_3k_aIgf_{\mathrm{PhI}}[\mathrm{Nu}]/k_{17}k_{-\mathrm{i}} \tag{22}$$

Mathematically, this has the same form as eq 21. However, it should be noted that in the derivation of eq 22 a cancellation of nucleophile concentration terms occurs inasmuch as the nucleophile is involved in both the relevant propagation and termination steps (3 and 17, respectively).

If initiation is governed by eq 20, propagation occurs as in Scheme I and termination is "unimolecular" in phenyl radical (with rate coefficient k_{u}), steady state derivation leads to eq 23.

$$dx/dt = k_3 Igf_{\mathrm{PhI}}[\mathrm{Nu}]/k_u \qquad (23)$$

This has the same mathematical form as eq 21 or 22. As mentioned above, both the initiation and termination steps involved in this model are improbable.

If initiation is governed by eq 19, propagation is correctly represented by Scheme I, and termination occurs by colligation of two phenyl radicals (eq 18); the rate law obtained by steady state derivation is that of eq 24.

$$dx/dt = k_3(k_a Igf_{\mathrm{PhI}}/2k_{-i}k_{18})^{1/2}[\mathrm{Nu}]^{3/2} \qquad (24)$$

This calls for the reaction to be half order in light intensity, three-halves order in nucleophile, and zero order in iodobenzene. Although the observed behavior (on the assumption that the iodobenzene-absorbed photons provoke reaction) does not comply with this rate law, the order in light intensity is somewhat less than one and the order in KDEP somewhat greater than one, indicating that termination bimolecular in radicals plays some role.

If the CT-absorbed photons are the ones that stimulate reaction, and if initiation occurs as in Scheme II, propagation as in Scheme I, and termination as in eq 16, one obtains the rate law

$$\frac{dx}{dt} = \frac{k_2 k_{14} Ig'f_{\mathrm{CT}}[\mathrm{Nu}]}{k_{16}(k_{-j} + k_{13} + k_{14}[\mathrm{Nu}])} \qquad (25)$$

From the same bases, but with termination as in eq 17, one derives eq 26, which is of the same form as eq 25.

$$\frac{dx}{dt} = \frac{k_3 k_{14} Ig'f_{\mathrm{CT}}[\mathrm{Nu}]}{k_{17}(k_{-j} + k_{13} + k_{14}[\mathrm{Nu}])} \qquad (26)$$

Again invoking Schemes I and II, but with termination as in eq 18, one obtains

$$\frac{dx}{dt} = k_3\left(\frac{k_{14}Ig'f_{\mathrm{CT}}}{2k_{18}}\right)^{1/2}\frac{[\mathrm{Nu}]^{3/2}}{(k_{-j} + k_{13} + k_{14}[\mathrm{Nu}]^{1/2})} \qquad (27)$$

This calls for half-order dependence on light intensity, and the observed 0.84-order dependence might be attributed to admixture of eq 27 to eq 25 or 26, owing to minor termination via step 18 alongside major termination via step 16 or 17. Such admixture would also perturb dependence on KDEP concentration as called for by eq 25 or 26, but the perturbation would be complex. Our data are not precise enough to enable judgment as to whether or not such perturbation occurs.

The Effects of Inhibitors. It is remarkable that dioxygen had no detectable effect on reaction rate. Similarly, in preparative experiments conducted in liquid ammonia solution, bubbling dry air through the reacting mixture was observed to have no deleterious effect on the yield of diethyl phenylphosphonate.[36]

Russell and Bridger[31] noted that the reactivity of phenyl radical toward dioxygen, relative to hydrogen atom abstraction from cyclohexane as a standard for comparison, is lower by several powers of ten than that of benzyl type radicals. Fu and Bentrude[38] observed that the reaction of PAT with trimethyl phosphite (TMP), a reaction that involves attack of phenyl radicals on TMP molecules, gives 95–98% yields of dimethyl phenylphosphonate under 1 atm of air, virtually the same as in a degassed system. The latter authors adduced evidence that the combination of phenyl radical with TMP to give initially the $\mathrm{PhP(OMe)_3}\cdot$ radical is very fast. Apparently the dioxygen molecule was not reactive enough to intercept an appreciable fraction of the phenyl radicals when in competition with TMP.

We believe that a similar explanation is applicable to the present case. The diethyl phosphite ion appears also to be exceedingly reactive with phenyl radical, so much so that dioxygen cannot interfere. Dioxygen also appears to be unable to steal electrons from the postulated iodobenzene and diethyl phenylphosphonate radical anion intermediates, either because such theft is thermodynamically unfavorable[39] or because it cannot compete kinetically with step 2 or 4, Scheme I.

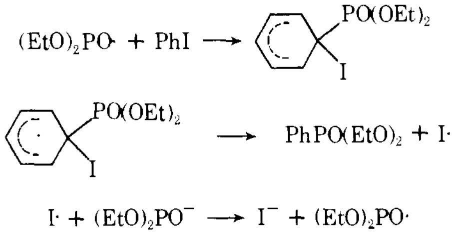
It is also noteworthy that the inhibitory effect of DEP molecules is quite mild; see, for example, set 45 or 49, Table I. Fu and Bentrude[38] similarly observed that dimethyl phosphonate, even when equimolar with TMP, reduced the yield of dimethyl phenylphosphonate on reaction with PAT only from about 98 to 88%. Dimethyl phosphonate is quite reactive as a hydrogen donor to the phenyl radical; its reactivity is 2.9 times that of $\mathrm{CCl_4}$ as a chlorine atom donor.[40] That makes dimethyl phosphonate more reactive than cumene as a hydrogen atom donor, and nearly as reactive as triphenylmethane.[20] The very modest effects of dimethyl phosphonate on the yield from reaction of PAT with TMP and on the quantum yield of reaction 1 testify further to the high reactivity of phenyl radical with TMP and with the diethyl phosphite ion, respectively.

The fact that 4.4 mole % of di-*tert*-butyl nitroxide reduced the rate of reaction 1 by only a factor of three is a further indication of the high reactivity of phenyl radical with diethyl phosphite ion.

Other Mechanisms. Heretofore we have discussed our findings entirely in terms of the radical chain mechanism with the propagation cycle shown in Scheme I. Our data, as well as other observations, are compatible with that mechanism. However, other possibilities must be examined.

One is a mechanism with the propagation cycle sketched in Scheme III.[41] Mechanisms more or less of this sort have been proposed for other radical reactions which effect replacement of halogen from aryl halides.[42,43]

Scheme III



Fields and co-workers[44] have shown that aromatic hydrocarbons and derivatives thereof are phosphonated upon reaction with refluxing DEP and di-*tert*-butyl peroxide; the reaction is believed to involve attack of $\mathrm{(EtO)_2PO}\cdot$ radicals on ring carbon atoms.[37b,44] That would constitute something of a precedent for the first step of Scheme III.

Strong evidence against the mechanism of Scheme III is the observation that an interrupted reaction of *m*-bromoiodobenzene with KDEP in ammonia (cf. ref 2 and 13) affords much tetraethyl *m*-phenylenebisphosphonate, much unreacted *m*-bromoiodobenzene, and little diethyl *m*-bromophenylphosphonate, coupled with observation that the bromophenylphosphonate ester is much less reactive with KDEP than is *m*-bromoiodobenzene.[45] These observations show that diethyl *m*-bromophenylphosphonate is not an intermediate on the main route to the bisphosphonate ester; cf. ref 3b. Inasmuch as iodobenzene is much more reactive than bromobenzene with KDEP, the mechanism of Scheme III would call for diethyl *m*-bromophenylphosphonate to be an intermediate in formation of the bisphosphonate ester.

Photochemical aromatic nucleophilic substitution in a number of nitro compounds and other substrates with nucleophiles such as cyanide ion and methoxide ion has been described especially by Cornelisse and Havinga[46] and Letsinger[47] and their co-workers. Mechanisms have been proposed which involve attack of a nucleophile on a photoexcited aromatic substrate, and which are not of chain character.

Those reactions seem quite different from that which is the subject of the present study. For one thing, their observed quantum yields are all less than unity.

Summary Comments. Our observation of quantum yields much greater than unity for reaction 1 demonstrates that it occurs by a chain mechanism. Our observation of an approximate first-order dependence of light intensity shows that termination is mainly unimolecular in propagating radical. There are also indications of a small fraction of termination by phenyl radical dimerization (step 18). Our data do not, however, define the initiation mechanism. They are consistent with either of two models: that initiation occurs through absorption of a photon by iodobenzene with ensuing reaction according to steps 8 and 9 or 8 and 10, or that it occurs through absorption of a photon by a charge-transfer complex of iodobenzene with diethyl phosphite ion with ensuing reaction as in Scheme II.

Some of our observed quantum yields, corrected for the fraction of the light absorbed by iodobenzene, are as high as 200 or higher (Table II). To estimate the kinetic chain length, the number of substitution events per initiation event, we must also know the quantum yield purely for initiation, which we do not know. If it were as low as 0.1, the kinetic chain length of reaction 1 would be 2000 or greater.

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Supplementary Material Available: Molar extinction coefficients of PhI and DEP (Table III), absorbances (Tables IV–VI), light intensity measurements (Table VII), quantum yields (Table VIII) and correlation of f_{CT}/Φ with 1/[KDEP] (Table IX) (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.
(2) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3612 (1974).
(3) (a) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3173 (1974); (b) *ibid.*, **39**, 3611 (1974).
(4) (a) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973); (b) *ibid.*, **38**, 3020 (1973).
(5) (a) J. F. Bunnett and J. E. Sundberg, *Chem. Pharm. Bull.*, **23**, 2620 (1975); (b) *J. Org. Chem.*, **41**, 1702 (1976).
(6) J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **39**, 382 (1974).
(7) J. F. Bunnett and X. Creary, unpublished experiments.
(8) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Am. Chem. Soc.*, **88**, 5662 (1966); N. Kornblum, *Angew. Chem.*, **87**, 797 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).
(9) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968).
(10) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970).
(11) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).
(12) (a) A. Levy, D. Meyerstein, and M. Ottolenghi, *J. Phys. Chem.*, **75**, 3350 (1971); (b) *ibid.*, **77**, 3044 (1973); (c) *Int. J. Appl. Radiat. Isot.*, **25**, 9 (1974).
(13) J. F. Bunnett, R. G. Scamehorn, and R. P. Traber, *J. Org. Chem.*, **41**, 3677 (1976).
(14) C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220**, 104 (1953); J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1960, pp 783–786.
(15) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971).
(16) J. H. Exner and E. C. Steiner, *J. Am. Chem. Soc.*, **96**, 1782 (1974).
(17) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
(18) E. S. Huyser, "Free-Radical Chain Reactions", Wiley-Interscience, New York, N.Y., 1970: (a) p 44; (b) p 51.
(19) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).
(20) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).
(21) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Am. Chem. Soc.*, **86**, 639 (1964); S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).
(22) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).
(23) P. D. Bartlett and R. Altschul, J. Am. Chem. Soc., **67**, 816 (1945).
(24) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions", 3rd ed, Part 1, E. S. Lewis, Ed., Wiley, New York, N.Y., 1974, p 381.
(25) J. Ferguson and T. Iredale, *J. Chem. Soc.*, 2959 (1953).
(26) M. Dzvonik, S. Yang, and R. Bersohn, *J. Chem. Phys.*, **61**, 4408 (1974).
(27) E. Olaerts and J. C. Jungers, *Discuss. Faraday Soc.*, **2**, 222 (1947).
(28) S. Hacobian and T. Iredale, *Nature (London)*, **166**, 156 (1950).
(29) R. A. Durie, T. Iredale, and A. H. Kingsbury, *Nature (London)*, **164**, 786 (1949); R. A. Durie, T. Iredale, and J. M. S. Jarvie, *J. Chem. Soc.*, 1181 (1950).
(30) R. K. Sharma and N. Kharasch, *Angew. Chem.*, **80**, 69 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 36 (1968).
(31) G. A. Russell and R. F. Bridger, *J. Am. Chem. Soc.*, **85**, 3765 (1963).
(32) M.-A. Fox, W. C. Nichols, Jr., and D. M. Lemal, *J. Am. Chem. Soc.*, **95**, 8164 (1973).
(33) L. O. Ruzo, N. J. Bunce, and S. Safe, *Can. J. Chem.*, **53**, 688 (1975); N. J. Bunce, S. Safe, and L. O. Ruzo, *J. Chem. Soc., Perkin Trans. 1*, 1607 (1975).
(34) R. A. Rossi and J. F. Bunnett, *J. Am. Chem. Soc.*, **96**, 112 (1974).
(35) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 90.
(36) J. F. Bunnett and R. P. Traber, unpublished work.
(37) W. G. Bentrude in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973; (a) p 612; (b) p 620.
(38) J.-J. L. Fu and W. G. Bentrude, *J. Am. Chem. Soc.*, **94**, 7710 (1972).
(39) Cf. R. Poupko and I. Rosenthal, *J. Phys. Chem.*, **77**, 1722 (1973).
(40) J.-J. L. Fu, W. G. Bentrude, and C. E. Griffin, *J. Am. Chem. Soc.*, **94**, 7717 (1972).
(41) We thank Dr. E. I. Heiba of Mobil Research and Development Corp. for discussion of mechanisms of this type.
(42) L. Benati, C. M. Camaggi, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 2817 (1972).
(43) J. R. Shelton and A. L. Lipman, Jr., *J. Org. Chem.*, **39**, 2386 (1974).
(44) E. K. Fields and R. J. Rolih, *Chem. Ind. (London)*, 999 (1960); E. F. Jason and E. K. Fields, *J. Org. Chem.*, **27**, 1402 (1962).
(45) J. F. Bunnett and S. J. Shafer, unpublished observations.
(46) J. Cornelisse and E. Havinga, *Chem. Rev.*, **75**, 353 (1975); J. Cornelisse, *Pure Appl. Chem.*, **41**, 433 (1975).
(47) W. C. Petersen and R. L. Letsinger, *Tetrahedron Lett.*, 2197 (1971), and earlier papers.