

Photochemically Induced Isotopic Exchange between Iodobenzene and Molecular Iodine

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The photochemical isotopic exchange between iodobenzene and radioactive molecular iodine ($I^{131}I$) was studied in methycyclohexane solutions. The limiting exchange yields, ϕ_{EX}^0 , measured at several excitation wavelengths in the uv range were found to be identical with the corresponding deiodination limiting yields, ϕ_{DE}^0 . This observation and a study of the effects of dissolved oxygen and iodine concentrations suggest that the exchange is initiated by photocleavage of iodobenzene to phenyl (Ph·) and iodine radicals, with O_2 and I_2 competing in the scavenging of Ph· ($k_{I_2+Ph\cdot}/k_{O_2+Ph\cdot} = 2.1 \pm 0.5$). The photocleavage of iodobenzene was found to be wavelength dependent in the near-uv range (e.g., 334 and 365 nm), where part of the absorption leads directly to the iodobenzene triplet. It is suggested that dissociation takes place from the lowest excited singlet, but practically not from the triplet state. It is shown that iodine atoms, produced by selective excitation in the visible range, do not exchange with iodobenzene. Neither does excitation of the charge-transfer (CT) complex between iodobenzene and iodine lead to exchange or deiodination.

Introduction

The isotopic exchange process $AI + I^*I \rightarrow AI^* + I_2$ where A is aliphatic, olefinic, or aromatic, can be induced by thermal, radiation-, or photochemical activation.¹⁻³ The mechanisms of the thermal³ and radiation^{4,5} induced exchange in aromatic iodides have been recently investigated and discussed. However, only partial and controversial information appears to be available concerning the corresponding photochemical exchange process. Such a process, first reported by Noyes,⁶ was later studied by Anbar and Rein⁷ who suggested the step $ArI + I^* \rightarrow ArI^* + I\cdot$ as the major exchange path. This conclusion appears to be inconsistent with observations (see ref 5 and later in this work) indicating that iodine atoms are unreactive with iodoaromatics.

In an attempt to elucidate the mechanism of the photochemical exchange, we have recently investigated the PhI- $I^{131}I$ system using monochromatic excitation at 365, 334, and 313 nm.⁸ The observed yields were found to be wavelength dependent but, under the corresponding experimental conditions ($[I_2] > 10^{-3} M$), they were not significantly affected by deaeration. Such observations induced us at the time to reject the dissociation $PhI \xrightarrow{h\nu} Ph\cdot + I\cdot$ as the step initiating the exchange process, favoring a mechanism involving an excited state of the PhI- $I^{131}I$ CT complex. This was supported by the wavelength dependence of the iodobenzene exchange yields, in contrast to those of the corresponding deiodination process which were assumed to be wavelength independent. Very recently

we have reexamined these conclusions in view of new experiments showing an oxygen effect on the exchange yields, detectable at low iodine concentrations. In the present work these new data are reported accompanied by a careful reinvestigation of the effects of wavelength, as well as those of oxygen and iodine, on the photodeiodination of iodobenzene. It will be shown that all observations lead to the formulation of a new reaction scheme for the photoexchange of iodine in iodoaromatics, involving phenyl radicals. The clarification of the photochemical exchange mechanism bears also on practical applications, such as the development of "clean" labeling techniques for aromatic iodides, free from by-products such as those associated with thermal or radiation-chemical methods.

Experimental Section

Materials. Iodobenzene (Aldrich Chemical Co.) was purified by vacuum distillation in an atmosphere of dry nitrogen. Light absorption at 365 nm was used for

- (1) R. M. Noyes and D. J. Sibbett, *J. Amer. Chem. Soc.*, **75**, 767 (1953).
- (2) R. K. Sharma and N. Kharasch, *Angew. Chem., Int. Ed. Engl.*, **7**, 36 (1968).
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- (4) A. Appleby, J. C. Charlton, and R. E. Spillett, *Chem. Commun.*, 958 (1967).
- (5) R. Riess and H. Elias, *J. Phys. Chem.*, **74**, 1014 (1970).
- (6) R. M. Noyes, *J. Amer. Chem. Soc.*, **70**, 2614 (1948).
- (7) M. Anbar and R. Rein, *Chem. Ind. (London)*, 1524 (1963).
- (8) A. Levy, D. Meyerstein, and M. Ottolenghi, *J. Amer. Chem. Soc.*, **92**, 418 (1970).

checking the purity of iodobenzene solutions in methylcyclohexane (ϵ_{PhI} at 365 nm, 0.13 ± 0.01). Iodine, resublimed (Fisher Scientific Co.), and methylcyclohexane (Matheson spectroquality) were used with no further purification.

Allyl iodide, used as a monitor of iodine atoms, was purified by the method described by Sibbett and Noyes.⁹

Iodine-131 carrier-free, in a basic aqueous iodide solution containing no reducing agents, was produced at the Nuclear Research Centre, Negev, by dry distillation of reactor-irradiated TeO_2 . Special care (using triply distilled water) was taken to ensure that the solution was free from organic impurities.

Light Source and Actinometry. Excitation wavelengths were selected from a medium pressure mercury arc by means of interference (Baird-Atomic Inc. λ 254, 313, and 334 nm). Corning glass (λ 365 nm with 0-52 and 7-37, and $\lambda > 520$ nm with 3-69) or Pyrex glass ($\lambda > 285$ nm) filters.

Actinometry in the uv range was performed using an uranyl oxalate actinometer. The rate of iodine atoms production by irradiation of iodine solutions in the visible range was evaluated using allyl iodide (0.1 M) as a selective iodine atom scavenger.¹⁰

Procedure. Solutions of radioactive iodine were prepared by shaking a 3-ml I_2 -methylcyclohexane solution for 5-10 min with about 1 ml of aqueous iodide-131 solution, to which 0.2 ml of 0.1 M H_2SO_4 and 0.1 ml of 0.01 M KIO_3 were previously added. The organic layer was separated and used for exchange experiments within 2 days. For each irradiation a sample of 0.5-1.5 mCi, or 0.5-1.5 μCi in the low activity samples, was employed. Solutions were deaerated by consecutive freeze and thaw cycles on a vacuum line. Oxygen concentrations were controlled by shaking the solution under the appropriate pressure of air. The exact amounts of dissolved oxygen were determined using gas-liquid chromatography on an 8-ft 13X molecular sieve column at 100°. At 23°, under a partial air pressure of 720 mm, the value of 3.4×10^{-3} M was obtained. After the irradiations, always carried out at room temperature, $24 \pm 1^\circ$, a known volume of the reaction mixture was shaken thoroughly for 10 min with a basic aqueous thiosulfate solution (0.1 M NaOH and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$). A part of the organic layer was then separated and counted in an ionization chamber (Mediac dose calibrator, Nuclear-Chicago) or in a well-type NaI(Tl) 2-in. crystal for the low activity samples. A blank, nonirradiated, sample was submitted to the same treatment, to account for thermal exchange. When low activity samples were used, iodine concentrations were determined spectrophotometrically before and after each irradiation. Exchange yields at 365 nm were found to be considerably affected by impurities, probably because of the very weak absorption of iodobenzene in this spectral range. This is apparently the

reason for the somewhat higher exchange yields reported previously at 365 nm.⁸

Deiodination yields were determined by measuring the optical density of the iodine photoproduct at 520 nm (ϵ_{I_2} 910), using a Hilger (Uvispek H 700) spectrophotometer.

Treatment of Data. The rate of exchange, R_{EX} , was calculated by applying McKay's equation¹¹ to our experimental conditions in which $[\text{PhI}] \gg [\text{I}_2]$, leading to

$$R_{\text{EX}} = \frac{2[\bar{\text{I}}_2] \ln \left(\frac{1}{1-F} \right)}{t} \quad (1)$$

where F is the exchange fraction and $[\bar{\text{I}}_2]$ is the average molar iodine concentration during the irradiation time t . This equation was used since the maximum increase in iodine concentration during a run was only 10%, while the change in iodobenzene concentration was of course negligible. Under these conditions, computation according to the method of Luehr, *et al.*,¹² which takes into account changes in the concentration of the reactants, does not give any improvement relative to the range of our experimental accuracy. The exchange quantum yield, Φ_{EX} , was determined by means of the expression

$$\Phi_{\text{EX}} = \frac{R_{\text{EX}}}{I_0 \alpha_x} \quad (2)$$

where I_0 is the intensity of light reaching the reaction cell (einstein/second, liter) and α_x is the light fraction absorbed by the photoactive species x , *e.g.*, identifying x with iodobenzene, we obtain $\alpha_{\text{PhI}} = D_{\text{PhI}}(\alpha_{\text{T}}/D_{\text{T}})$ where D_{T} and α_{T} are, respectively, the total optical density and the total light fraction absorbed. The corresponding expression for the deiodination process is

$$\Phi_{\text{DE}} = \frac{R_{\text{DE}}}{I_0 \alpha_x} = \frac{2\Delta[\text{I}_2]}{t(I_0 \alpha_x)} \quad (3)$$

where $\Delta[\text{I}_2]$ is the increment in the iodine concentration at time t .

Results and Discussion

1. *Excitation within the Visible I_2 Band.* In order to check the role of iodine atoms produced as the only reactive radicals in the $\text{PhI-I}^{131}\text{I}$ system, we have submitted deaerated iodobenzene- I^{131}I solutions in methylcyclohexane to visible light excitation. A 3-69 Corning glass filter was employed to transmit light above 520 nm, in the range of the iodine absorption

(9) D. J. Sibbett and R. M. Noyes, *J. Amer. Chem. Soc.*, **75**, 761 (1953).

(10) (a) F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954); (b) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

(11) See A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," Wiley, New York, N. Y., 1951, p 7.

(12) C. P. Luehr, G. E. Challenger, and B. J. Masters, *J. Amer. Chem. Soc.*, **78**, 1314 (1956).

band. The iodobenzene concentration was 0.1 *M* and that of the iodine carrier was varied in the 7×10^{-5} to 8×10^{-4} *M* range. Under these conditions light is exclusively absorbed by molecular iodine leading to iodine atoms. No photochemically induced pickup of radioactive iodine by iodobenzene could be detected, even after prolonged irradiations. From the yields of iodine atoms production, estimated by means of the allyl iodide technique,¹⁰ an upper limit of $\phi_{\text{EX}} < 10^{-5}$ was determined for the exchange induced by excitation within the visible I_2 band. We may therefore conclude that iodine atoms as such do not play a detectable role in the photochemical process. This conclusion, in agreement with a previous suggestion of Riess and Elias,⁵ rules out the exchange process ($\text{ArI} + {}^{131}\text{I} \cdot \rightarrow \text{Ar}^{131}\text{I} + \text{I} \cdot$) suggested by Anbar and Rein⁷ for alcoholic solutions. An alternative path: $\text{ArI} \cdot \text{I}^{131}\text{I} + \text{I} \cdot \rightarrow \text{Ar}^{131}\text{I} \cdot \text{I}_2 + \text{I} \cdot$, involving a reaction between an iodine atom and an iodobenzene-iodine CT complex, is also ruled out in our systems by the present experimental data. Such a mechanism has been recently proposed by Milligan and coworkers to account for the closely related photochemical interchange of halogens between haloaromatics and halogen molecules in solution.¹³

2. *Exchange and Deiodination Induced by Uv Irradiation.* As previously reported^{2,6,8} uv irradiation of iodobenzene-iodine systems leads to a substantial exchange of iodine. As expected from a simple exchange process, the radioactivity of the aromatic material was found to be proportional to the initial iodine radioactivity. The exchange rate exhibited the characteristic exponential dependence on the irradiation time, and the equilibrium value $[\text{PhI}^*]_{\infty}$ (*i.e.*, the maximum radioactivity obtainable in iodobenzene) was found to be consistent with the expected value

$$[\text{PhI}^*]_{\infty} = [\text{II}^*]_0 \frac{[\text{PhI}]}{[\text{PhI}] + 2[\text{II}]} \quad (4)$$

where $[\text{II}^*]_0$ is the initial concentration of radioactive iodine.

Using a Pyrex glass filter, transmitting above 285 nm, photochemical experiments were carried out in 3.0×10^{-2} *M* iodobenzene-methylcyclohexane solutions in the presence of 1.1×10^{-4} to 4.4×10^{-4} *M* molecular iodine. Under such experimental conditions the principal uv mercury lines absorbed by the solutions are those at 303 and 313 nm with only a small contribution ($\sim 20\%$) from the 334-nm line and a negligible one (less than 2%) from that at 365 nm. The irradiated solutions were tested for both exchange and deiodination, as functions of oxygen and iodine concentrations. Exchange yields, unaffected by $[\text{O}_2]$ at relatively high iodine concentrations, were found to be markedly affected by either $[\text{O}_2]$ or $[\text{I}_2]$, when both values fell within the proper 8×10^{-5} to 8×10^{-4} *M* range. Explicitly, R_{EX} increases with increasing $[\text{I}_2]$ but is lowered by dissolved oxygen (see Figure 1). As to de-

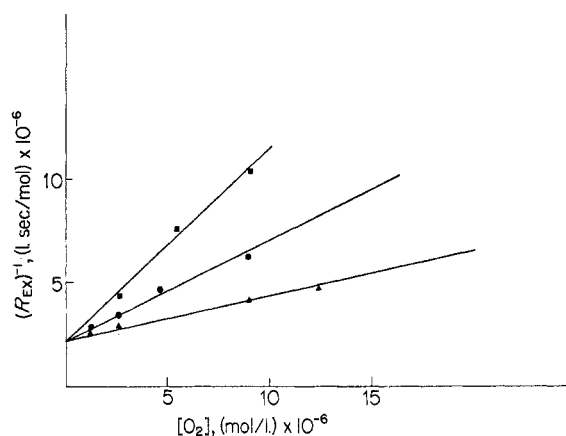


Figure 1. Reciprocal exchange rates $(R_{\text{EX}})^{-1}$ as function of the oxygen concentration in 0.03 *M* solutions of PhI in methylcyclohexane: ■, $[\text{I}_2] = 1.1 \times 10^{-4}$ *M*; ●, $[\text{I}_2] = 2.3 \times 10^{-4}$ *M*; ▲, $[\text{I}_2] = 4.4 \times 10^{-4}$ *M*. Excitation was polychromatic as described in the text.

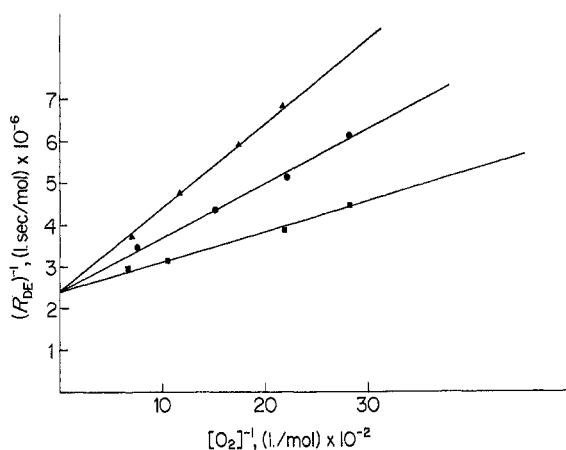
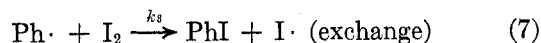
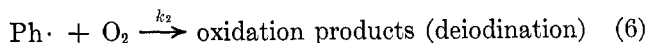
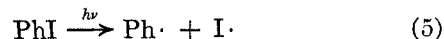


Figure 2. Reciprocal rates of deiodination $(R_{\text{DE}})^{-1}$ plotted vs. $[\text{O}_2]^{-1}$ in 0.03 *M* solutions of PhI in methylcyclohexane: ■, $[\text{I}_2] = 1.2 \times 10^{-4}$ *M*; ●, $[\text{I}_2] = 2.5 \times 10^{-4}$ *M*; ▲, $[\text{I}_2] = 3.3 \times 10^{-4}$ *M*. Excitation was polychromatic as described in the text.

iodination rates, R_{DE} , they were found to exhibit oxygen and iodine concentrations effects, opposite to those of R_{EX} (Figure 2). Such observations, indicating that exchange and deiodination are essentially two competing processes, suggest the validity of the simple scheme



to account for the effects of oxygen and iodine. The scheme leads to the expressions

(13) J. T. Echols, V. T. C. Chuang, C. S. Parrish, J. E. Rose, and B. Milligan, *J. Amer. Chem. Soc.*, **89**, 4081 (1967).

$$R_{DE} = R_{DE}^0 \frac{k_2 [O_2]}{k_2 [O_2] + k_3 [I_2]} \quad (8)$$

$$R_{EX} = R_{EX}^0 \frac{k_3 [I_2]}{k_3 [I_2] + k_2 [O_2]} \quad (9)$$

where R_{DE}^0 is the deiodination rate when $[O_2] \gg [I_2]$ and R_{EX}^0 is the exchange rate when $[I_2] \gg [O_2]$.

The applicability of these equations to our experimental data is tested in Figure 1 where $1/R_{EX}$ is plotted vs. $[O_2]$, and in Figure 2 where $1/R_{DE}$ is plotted against $1/[O_2]$. A linear behavior is obtained in both cases for various iodine concentrations in the 1.1×10^{-4} to $4.4 \times 10^{-4} M$ range. In each figure a common intercept is obtained for lines of different $[I_2]$ values, and the same rate constants ratio, $k_3/k_2 = 2.2 \pm 0.3$, is calculated from each line in either Figure 1 ($k_3/k_2 = \text{intercept/slope } [I_2]$) or Figure 2 ($k_3/k_2 = \text{slope/intercept } [I_2]$). From the corresponding intercepts, R_{EX}^0 and R_{DE}^0 were calculated leading to the yield ratio: $(\phi_{EX}^0/\phi_{DE}^0) = 1.04 \pm 0.06$. We may thus conclude that the experimental data are in complete agreement with the mechanism consisting of reactions 5-7. The role of iodine as a phenyl radical scavenger, which has been a matter of some controversy,^{2,4,14} is now clearly established.

We have previously ruled out any significant role of iodine atoms produced from the photolysis of I_2 in the exchange process. We may still question, however, their role when produced from the photolysis of iodobenzene. This point is relevant to the recent radiation-chemical work of Reiss and Elias in which the reaction



(where PhI^\ddagger is an unidentified excited state of iodobenzene) has been suggested as the major exchange step. When photolyzing PhI , both iodine atoms and excited iodobenzene molecules may be present to allow the proposed reaction. However, the kinetic analysis presented above, showing that I_2 and O_2 compete in the scavenging of the same intermediate, is inconsistent with the above step. Also, the mechanism involving PhI^\ddagger will not explain the identity between ϕ_{DE}^0 and ϕ_{EX}^0 , and can therefore be rejected in our photochemical system in favor of the scheme of reactions 5-7.

Experiments similar to the above were also performed using monochromatic excitation at 254, 313, 334, and 365 nm. The values obtained for the ratios k_3/k_2 (2.1 ± 0.5) and ϕ_{EX}^0/ϕ_{DE}^0 (1.00 ± 0.06) were practically identical with those reported above for the polychromatic light. However, in the monochromatic cases, absolute values for ϕ_{EX}^0 (and ϕ_{DE}^0) could also be calculated. The values obtained taking α_x as the light fraction absorbed by iodobenzene at each wavelength (see Experimental Section) are presented in Table I. It is of interest to point out that the quantum yields for deiodination of iodobenzene in the above spectral re-

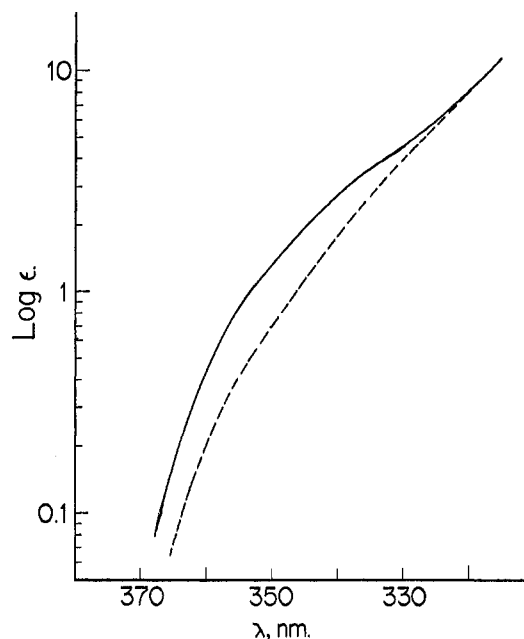


Figure 3. Long wavelength range of iodobenzene absorption in methylcyclohexane, measured at $[PhI] = 0.1-1 M$. Continuous line is experimental spectrum, dotted line is a rough estimate of the separate contribution of the $S_0 \rightarrow S_1$ transition. The difference between the curves is attributed to the direct $S_0 \rightarrow T_1$ absorption (see also ref 16).

gion are currently assumed to be very close to unity.^{2,15} Our data for methylcyclohexane solutions at room temperature appear to be in better agreement with the early work of Olaerts and Jungers,¹⁶ who report a maximum value of 0.37 for the quantum yield of the deiodination process.

Table I: Deiodination and Exchange Quantum Yields for Methylcyclohexane Solutions at Room Temperature ($24 \pm 1^\circ$)

Wave-length, nm	Iodo-benzene concentration, mol/l.	Iodine concentration, mol/l.	ϕ_{DE}^0	ϕ_{EX}^0
254	0.001	$2-6 \times 10^{-4}$	0.39 ± 0.02	0.39 ± 0.02
313	0.03	$2-7 \times 10^{-4}$	0.39 ± 0.02	0.39 ± 0.02
334	0.1-0.5	$1-6 \times 10^{-4}$	0.30 ± 0.02	0.30 ± 0.02
365	0.1-0.5	$1-6 \times 10^{-4}$	0.22 ± 0.02	0.22 ± 0.02

As mentioned above, the identity between ϕ_{DE}^0 and ϕ_{EX}^0 presents the main evidence for the exchange mechanism initiated by the photocleavage of iodobenzene. As shown in Table I, ϕ_{DE}^0 and ϕ_{EX}^0 are independent of $[I_2]$. Recalling that both parameters were calculated

(14) J. F. Garst and R. S. Cole, *Tetrahedron Lett.*, **11**, 679 (1963).

(15) See J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1967, p 528.

(16) E. Olaerts and J. C. Jungers, *Discuss. Faraday Soc.*, **2**, 222 (1947).

assuming that PhI is the photoactive species (*i.e.*, $x \equiv \text{PhI}$), this second observation yields additional evidence in favor of the exchange being initiated by light absorption of iodobenzene. Assuming the alternative mechanism, involving light absorption by the $\text{PhI} \cdot \text{I}_2$ charge-transfer complex (*i.e.*, $x \equiv \text{PhI} \cdot \text{I}_2$), the same experimental data will lead to a marked dependence of the exchange yields on $[\text{I}_2]$, a fact for which it will be difficult to account reasonably. We therefore attribute all photoprocesses to the excitation of PhI, concluding that the charge-transfer complex is photochemically inactive.

Attention should now be paid to the marked drop in the quantum yields observed upon increasing the excitation wavelengths to 334 and 365 nm. Such effects should be considered in view of the characteristic absorption spectrum of iodobenzene in this region. It has been pointed out by Ferguson and Iredale¹⁷ (see also Figure 3) that concentrated iodobenzene solutions exhibit a distinct shoulder around 350 nm. Their low-temperature phosphorescence experiments strongly suggested that this low-energy band should be attributed to the $S_0 \rightarrow T_1$ transition. A rough estimate gives 0.5 and 0.8 for the intensity ratio $\epsilon_{(S_0 \rightarrow S_1)} / [\epsilon_{(S_0 \rightarrow S_1)} + \epsilon_{(S_0 \rightarrow T_1)}]$ at 365 and 334 nm correspondingly. These two numbers should be compared with the limiting deiodination yields ratios: $[\phi_{\text{DE}}^0(365 \text{ nm}) / \phi_{\text{DE}}^0(254 \text{ nm})] = 0.56$ and $[\phi_{\text{DE}}^0(334 \text{ nm}) / \phi_{\text{DE}}^0(254 \text{ nm})] = 0.77$. The same values (see Table I) are ob-

tained for the corresponding limiting exchange yields. Recalling that at 254 nm $\epsilon_{(S_0 \rightarrow S_1)} \gg \epsilon_{(S_0 \rightarrow T_1)}$, the matching within each of the two pairs means that the limiting deiodination or exchange yields are proportional to the population of S_1 , and that the lowest triplet state does not undergo a detectable photodissociation at room temperature.

Thus, the photochemistry of iodobenzene in the 250–400-nm range is only due to light absorption within the $S_0 \rightarrow S_1$ band which leads to dissociation into $\text{Ph} \cdot$ and $\text{I} \cdot$ radicals, with phenyl radicals reacting with both iodine and oxygen. Under our particular experimental conditions we have found no evidence for their reaction with iodobenzene, as recently suggested for aqueous solutions.¹⁸ These results seem to clarify some controversy concerning the mechanism of radiolytically induced exchange in iodoaromatics^{4,5} supporting the scheme involving a reaction between I_2 and $\text{Ph} \cdot$ as suggested by Appleby, Charlton, and Spillett for aqueous solutions.⁴

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(17) J. Ferguson and T. Iredale, *J. Chem. Soc.*, 2959 (1953).

(18) B. Cercek and M. Kongshaug, *J. Phys. Chem.*, **74**, 4319 (1970).