Photochemical Reactions of Iodine with Carbon–Hydrogen Bonds at 90° and 300°K. and Above and Below the 4995 Å. Convergence Limit[1]

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The evidence obtained in this work indicates that the bleaching of solutions of iodine in glassy EPA at 90°K. by irradiation with visible light is primarily the result of chemical reactions which produce hydrogen iodide. Color reappears on warming as a result of triiodide formation and of oxidation of HI. Electron spin resonance measurements on glassy solutions of iodine in ethyl alcohol, ethyl ether and isopropyl alcohol at 77°K. show that in each of these systems trapped free radicals are formed by photochemically activated iodine abstracting secondary hydrogen atoms. These radicals undergo internal rearrangement on standing at 77°K. When iodine in liquid ethyl alcohol, ethyl ether or isopentane at room temperature is exposed to visible light it disappears. In the alcohol and ether this disappearance is accompanied by the growth of triiodide absorption bands at 3600 and 2900 Å., which pass through a maximum and then decrease with continued irradiation. This decrease is accompanied by appearance of absorption at about 2200 Å. which is ascribed to a charge transfer complex of HI. Exposure of the resultant solutions to air leads to gradual conversion of the HI back to triiodide and subsequently to iodine. Irradiation of iodine vapor in propane at 49° with light at either 5125 Å. (above the convergence limit) or 4790 Å. (below the convergence limit) produces both i-C$_3$H$_7$I and n-C$_3$H$_7$I with quantum yields of about 2×10^{-4} for each. Consideration of the evidence favors a mechanism in which a collision complex RH $\cdots$ I occasionally reacts with an I atom to form RI + HI rather than RH + I$_2$.

Introduction

Norman and Porter[2] have observed that 10^{-4} M iodine dissolved in EPA[3] glass at 77°K. can be bleached by irradiation with visible light. On warming, the color of the iodine reappeared accompanied by the absorption spectrum of hydrogen triiodide. This experiment has been interpreted[4a,b] as showing the production of trapped iodine atoms and has been of interest in relation to the rapidly growing information[4] on matrix stabilization techniques for storing free radicals.

From previous work in our Laboratory[5] in which the photolysis of ethyl iodide was studied in condensed phases at 2537 Å., the extrapolated quantum yield for the escape of C$_2$H$_5$ radicals from I atoms at 93°K. can be calculated to be 0.0005. If the quantum yield for the formation of trapped iodine atoms by the photolysis of I$_2$ in EPA at 77°K. were this low, it could not account for the bleaching observed. The possibility that a photochemical reaction of iodine with the alcohol of EPA might contribute to the bleaching is suggested by the absorption spectra of alcohol solutions of iodine which have been irradiated with visible light.[6]

To clarify the nature of the bleaching process and to investigate the generality of photochemical reactions of iodine with saturated molecules, we have determined the absorption spectrum of bleached solutions of iodine in EPA at liquid air temperatures, and the electron spin resonance spectra of irradiated solutions of iodine in ethanol, in ethyl ether and in 2-propanol at 77°K. Additional observations have been made on the growth and disappearance of ultraviolet absorption due to HI, HI$_3$ and I$_2$ resulting from irradiation and subsequent oxidation of solutions of I$_2$ in each of the components of EPA at room temperature. To assist in identifying the photochemically produced iodine species which attack the carbon–hydrogen bond, we have studied the reaction between iodine and propane in the gas phase when activated by light above and below the convergence limit of iodine.

Experimental

Materials.—Phillips' Pure Grade isopentane was stirred for several hours at 0° with concentrated sulfuric acid to remove olefinic impurities and was then washed with a solution of sodium carbonate, dried over magnesium sulfate and fractionally distilled on a Todd Column packed with glass helices, a center fraction being retained. Mallinckrodt anhydrous A.R. ethyl ether was stored over sodium. Absolute ethanol from Commercial Solvents Corporation, and Phillips Research Grade isobutane, propane, ethane and methane were used as received. Fisher Scientific Company Certified Reagent 2-propanol was used as received.

Sample Preparation.—When EPA was used as solvent, the components were mixed immediately before use, and 5 ml. was pipetted into a small tube which was connected to a vacuum line with a standard taper joint. The EPA was thoroughly degassed by several cycles of freezing, pumping and thawing and then vacuum distilled through magnesium sulfate into a square quartz cell of 10 mm. optical path. An aliquot of a potassium iodide (Mallinckrodt Analytical Reagent) solution was evaporated to dryness in a Pyrex tube. A small amount of potassium dichromate was added, the tube was sealed onto the vacuum line and heated until the potassium iodide was oxidized to iodine, which was then distilled through magnesium sulfate into the quartz optical cell containing the EPA. Greater than 95% of the iodine could be transferred this way. The same procedure was employed in preparing samples of iodine in ethanol alone. The preparation of solutions of iodine in isopentane and in ethyl ether was similar except that each solvent was distilled through phosphorus pentoxide instead of magnesium sulfate.

Samples for electron spin resonance measurements were vacuum distilled into 4 mm. o.d. quartz tubes.

To prepare hydrogen iodide, a mixture of solid 55% aqueous hydriodic acid (Merck Reagent Grade) and phos-

(1) (a) Presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, August, 1961. (b) More complete details of this work are available in the Ph.D. thesis of S. V. Filseth filed with the University of Wisconsin library in 1962. It may be obtained from University Microfilms, Ann Arbor, Michigan.

(2) I. Norman and G. Porter, *Proc. Roy. Soc.* (London), A230, 399 (1955).

(3) A mixture of ethyl ether, isopentane and ethyl alcohol in a volume ratio of 5:5:2.

(4) (a) A. M. Bass and H. P. Broida, "Formation and Trapping of Free Radicals," Academic Press, Inc., New York, N. Y., 1960. (b) G. J. Minkoff, "Frozen Free Radicals," Interscience Publishers, Inc., New York, N. Y., 1960. (c) NBS Monograph 12, "Stabilization of Free Radicals at Low Temperatures," U. S. Govt. Printing Office, Washington, D. C., 1960. (d) J. L. Franklin and H. P. Broida, "Trapped Energetic Radicals," in *Annual Review of Physical Chemistry*, Vol. X, Annual Reviews Inc., Palo Alto, 1959.

(5) R. H. Luebbe, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, 81, 761 (1959).

(6) A. Bately, *Trans. Faraday Soc.*, 24, 438 (1928).

phorus pentoxide at liquid air temperature was warmed on the vacuum line. The hydrogen iodide gas was passed through phosphorus pentoxide and subjected to several trap to trap fractionations at −78° before condensing into a cell.

Experiments on the photochemical reaction of iodine with propane, ethane and methane were carried out in cylindrical quartz cells 2.5 cm. in diameter with 10 cm. optical paths. The degassed hydrocarbons were stored on the vacuum line in 3 liter bulbs behind stopcocks greased with Kel-F fluorocarbon lubricant. Samples for individual experiments were metered by pressure–volume measurements in a calibrated volume using a mercury manometer. Iodine was added using the KI–K$_2$Cr$_2$O$_7$ technique. For experiments with added I^{131}, a small amount of carrier-free KI^{131} was added to the aliquot of inactive KI.

Apparatus and Techniques.—High intensity irradiations of EPA glasses which were to be analyzed spectrophotometrically were carried out in a Pyrex Dewar designed so that the optical cell, immersed in liquid nitrogen, could be placed within 13 mm. of the capillary of a 1000 watt AH6 mercury arc, with 5 mm. of a circulating CuSO$_4$ filter solution (100 g./l.) between the arc and the cell. A constricted finger, which held the cell near the light, projected below a larger coolant reservoir of the Dewar. The cross section of the inner tube of this finger was square except for the side opposite the incoming light which was cylindrical for the purpose of reflecting light backi nto the sample. The vacuum annulus of the Dewar was completely silvered except for a section on the side where the light entered. The outer as well as the inner tube was flattened on this side. It was found that optical cells immersed in liquid nitrogen in this Dewar gradually accumulated a coating of ice crystals on the faces. In the experiments to be reported this was avoided by coating each face with a thin film of dichlorodimethylsilane prior to cooling. Lower intensity irradiations were carried out in the cryostat described previously.[7] This cryostat was also used for examining the spectra of glasses at liquid air temperature with the aid of a Cary or Beckman spectrophotometer.

For the gas phase experiments, in which it was desired to use light in narrow wave length ranges, the light from the AH6 arc was passed through a Farrand UV–VIS grating monochromator with a 100–150 Å. band pass. The amount of light absorbed by the iodine–hydrocarbon reaction mixtures in each wave length range used with the monochromator was evaluated from uranyl oxalate actinometry,[8] carried out at 4210 Å., by applying appropriate factors for actinometer and sample absorbancy and arc output as a function of wave length. An aluminum block oven was used to maintain the gaseous samples at 49° during irradiation. Radioactive organic iodides produced by irradiation of iodine (I^{131})–hydrocarbon mixtures were separated by gas chromatography using a 12 foot spiral column packed with 40–60 mesh firebrick coated with GE SF-96(40) silicone oil. Elemental iodine was removed from the reaction products by retaining it in a trap at −45° while the unreacted hydrocarbon and products were vaporized and condensed at liquid air temperature into the small bulb which was to be sealed off and broken on the chromatography column. Hydrogen iodide was removed by a short section of Amberlite IRA-400 ion exchange resin which preceded the column. The outlet from the column was connected to a U-tube which fit into the well of a NaI(Tl) scintillation crystal which detected the RI(I^{131}) products as they appeared in the effluent. Absolute photochemical yields of the RI products were determined by calibrating peak areas on the recorder activated by the scintillation counter, using CH$_3$I(I^{131}) of known specific activity prepared by photochemical exchange of I$_2$(I^{131}) with CH$_3$I. Electron spin resonance measurements were carried out at 77°K. with a Varian V-4500 reflection type X-band spectrometer employing 100 kc. field modulation.

Results

Photochemical Reaction of Iodine in EPA Glass.

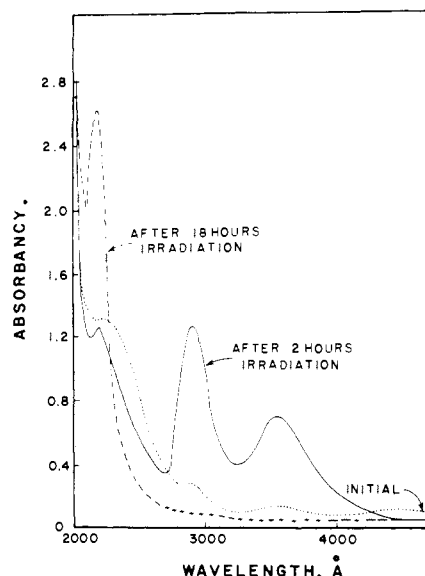When a 10^{-4} M solution of iodine in EPA glass was irradiated at 90°K. with an AH6 1000 watt

(7) T. O. Jones and J. E. Willard, *Rev. Sci. Inst.*, **27**, 1037 (1956).

(8) J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor and W. Brim, *J. Am. Chem. Soc.*, **77**, 5499 (1955).

Fig. 1.—Spectral changes produced by irradiation at 25° of 10^{-4} M I$_2$ in C$_2$H$_5$OH with visible light (AH6 arc at distance of 3 cm. from 1 cm. thick reaction cell; light filtered by Pyrex and 5 mm. of 100 g./l. CuSO$_4$).

mercury arc 13 mm. from the face of the cell, and with the CuSO$_4$ filter intervening, complete visual bleaching of the iodine color was achieved in 1 hr. No reappearance of color occurred when such samples were allowed to stand for several hours at liquid air temperature. Spectrophotometric observation of the irradiated sample at 90°K. showed strong absorption in the ultraviolet with maxima at 2910 and 3580 Å. due to triiodide. On melting the glass and warming to room temperature visible color due to the long wave length tail of the 3580 Å. peak of triiodide appeared. In one experiment, where the spectrum of the glass was not determined, the absorption at 3580 Å. was low immediately after melting, grew slowly at room temperature, passed through a maximum and then decreased, while in two other experiments it increased sharply during the process of melting and then decreased slowly with simultaneous appearance and growth of the absorption band of molecular iodine, which has a maximum at 4450 Å. in ethanol. It is probable that the iodine in the first sample had been converted completely to HI, which does not absorb at 3580 Å. or in the visible region of the spectrum and which was slowly oxidized to triiodide, as discussed below. The very rapid increase in absorption at 3580 Å. on melting the last two samples may be ascribed to complexing of HI with small unreacted amounts of I$_2$—a reaction which can occur rapidly in the liquid but not in the glass at 90°K. This complexing would lead to a marked increase in visible color due to the fact that the long wave length tail above 4000 Å. of the 3580 Å. triiodide band has an appreciably higher absorbancy than an equivalent concentration of iodine (see Fig. 1).

The growth of the triiodide peaks after melting the completely bleached glass, and their subsequent conversion to the iodine peak in all three samples cited above, must be due to a difficultly removable
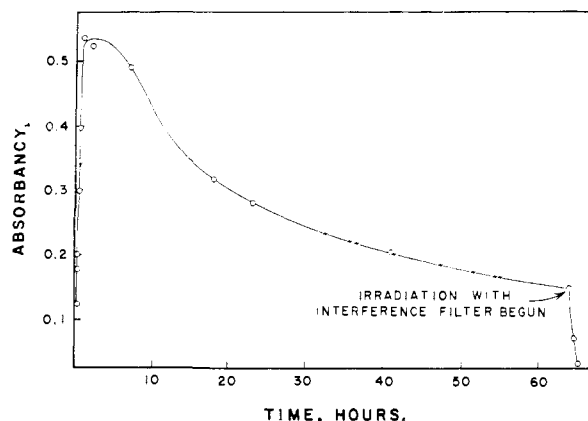
Fig. 2.—Absorbancy at 3550 Å. as a function of time of irradiation at 25° of a 10^{-4} M solution of I_2 in C_2H_5OH; Corning 3389 filter, opaque below 4000 Å., used for first 64 hr. after which it was replaced by an interference filter with maximum transmission at 3550 Å.

oxidizing impurity. The fact that permanent bleaching was achieved with solutions of iodine in EPA irradiated at room temperature, as described below, shows that the impurity can be removed by prolonged irradiation.

Photochemical Reaction of Iodine with Liquid EPA, Ethanol, Ethyl Ether and Isopentane.—The photochemical reaction of 10^{-4} M I_2 with each of the three solvents, EPA, ethanol and ethyl ether at room temperature, has been investigated by spectrophotometric observation of the solutions before, during and after irradiation at a distance of 3 cm. from an AH6 arc filtered by 5 mm. of 100 g./l. $CuSO_4$ solution. In each case, during about 1 hr. of irradiation, the absorbancy at 2900 and 3600 Å. increased rapidly, passed through a maximum and then fell off slowly to zero. These changes were accompanied by the disappearance of the I_2 absorption band in the visible region of the spectrum and the growth of absorption peaks with maxima at 2170, 2160 and 2270 Å. for EPA, ethyl alcohol and ethyl ether, respectively. This is illustrated in Fig. 1 for an irradiation at somewhat lower intensity and longer duration.

The new species which is formed in the oxygenated solvents was identified as hydrogen iodide since independently prepared solutions of hydrogen iodide in ethyl ether exhibited an absorption maximum at 2270 Å. In the case of each of the oxygenated solvents the absorbancy index of the species which absorbed in the 2200 Å. region was much higher than that of the I_2 from which it was produced (Fig. 1). This observation suggests that the absorbing species is a charge transfer complex between the HI and the solvent, since, in the gas phase, the absorbancy index of HI at its maximum is only about one third that of I_2 at its maximum. Consistent with this conclusion is the fact that when the iodine color is bleached by photolysis in a non-oxygenated solvent such as isopentane (see below), no absorption appears in the 2200 Å. region within the sensitivity of the measurements made.

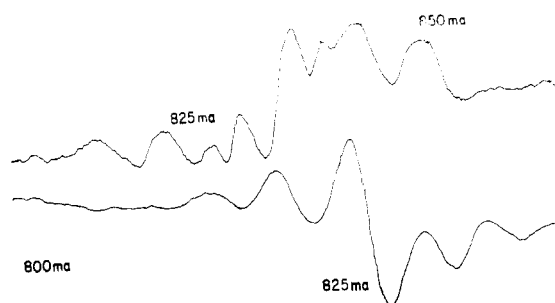An experiment was done to determine whether radiation absorbed by iodine and radiation ab-

Fig. 3.—Electron spin resonance spectra of 4×10^{-3} M I_2 in C_2H_5OH in quartz sample tube after irradiation at 77°K. in Pyrex Dewar with AH6 arc: upper spectrum, immediately after irradiation; lower spectrum, same sample after standing two days at 77° K.

sorbed by triiodide are independently able to cause HI production. A 10^{-4} M solution of iodine in ethanol was first irradiated with the AH6 arc filtered by a Corning 3389 filter which is essentially opaque below 4000 Å. The light transmitted by the filter was in the region of maximum absorbancy of molecular iodine but included only the high wave length, low absorbancy, tail of the triiodide absorption. The absorbancy of the 3550 Å. peak as a function of time during this irradiation (which was done with the arc at a distance of 10 cm. from the sample) is shown in Fig. 2. After 64 hr. of irradiation there was no detectable absorption by molecular iodine at 4450 Å. An interference filter with maximum transmission at the 3550 Å. peak of triiodide absorption was then substituted for the Corning filter, with the result, as shown in Fig. 2, that bleaching of the 3550 Å. absorption was greatly accelerated.

When bleached solutions having an absorption spectrum such as the dashed line of Fig. 1 were opened to the air, color reappeared. The peak at 2160 Å. decreased with time simultaneously with increase to a maximum and subsequent decay of absorbancy at 2870 and 3550 Å. After prolonged standing the spectrum was identical with that of the solid line which had been observed prior to irradiation. This behavior is ascribed to air oxidation of HI to I_2.

When 10^{-4} M solutions of iodine in isopentane were irradiated with the AH6 arc, they were bleached, although more slowly than the solutions described above. The absorbancy due to iodine in the 5200 Å. region disappeared, but in contrast to the alcohol and ether solutions no new absorption bands appear. The 5200 Å. absorption band reappeared when the bleached solutions were exposed to air.

Observation of Free Radicals Produced by Photochemical Reaction of I_2 with Ethanol, Ethyl Ether and 2-Propanol.—A 4×10^{-3} molar solution of iodine in ethanol glass was irradiated at 77°K. for 2 hr. in Pyrex with the full light of the AH6 arc at a distance of 35 mm. The electron spin resonance spectrum obtained from this sample immediately after irradiation is shown in Fig. 3, together with the spectrum of the same sample after standing for two days in liquid nitrogen. Similar treatment of a glassy solution of iodine in

ethyl ether led to an initial spectrum shown at the top of Fig. 4 which, on standing, for two days at 77°K., was also replaced by a five line pattern. Also shown in Fig. 4 is the spectrum obtained from an irradiated solution of I_2 in 2-propanol. Similar attempts to observe free radicals in the I_2–isopentane system were unsuccessful, perhaps because of the very low solubility of I_2 in saturated paraffinic hydrocarbons.

Photochemical Reaction of I_2 with Propane in the Gas Phase.—Studies of the reactions of hydrocarbons with iodine activated by visible light in the gas phase were undertaken because they offered the possibility of determining whether the excited iodine molecules formed above the spectroscopic band head at 4995 Å. showed different reactivity than the $^2P_{1/2}$ atoms formed at wave lengths below the band head.

Preliminary experiments in which mixtures of about 100 mm. of either isobutane or propane with 1 mm. of iodine were irradiated at 49° in close proximity to the AH6 arc, filtered only by its Pyrex jacket, produced a reddish-brown deposit on the walls of the reaction cell after several hours of irradiation. This deposit transferred readily to a side arm on the cell when the latter was cooled with liquid air. After dissolving the deposit from the isobutane experiment in isopentane and removing the elemental iodine by shaking with a drop of mercury, the solution gave an absorption spectrum with maxima at 2200 Å., the region in which hydrogen iodide absorbs, and at 2680 Å., which is the absorption maximum of tertiary butyl iodide. Hydrogen iodide is known to adsorb on glass and quartz surfaces strongly. It is speculated that the colored deposit may be an adsorbed complex of iodine and hydrogen iodide. The same type of deposit was observed in runs using light passed by a Corning 3484 filter, which transmits primarily in the wave length region above the convergence limit and in runs using a Corning 5850 filter which transmits only below the convergence limit.

Following these preliminary experiments, a series of experiments on gaseous mixtures of 1.2 mm. of iodine with about 125 mm. of propane at 49° was carried out using the monochromator to select a 100–150 Å. band at 4790 Å. in some cases and in others a similar band at 5125 Å. The iodine was labelled with I^{131}. Following irradiations of about 6 hr. the residual iodine was removed from the rest of the reaction mixture by condensation at −45°, and the remainder of the mixture was analyzed by gas chromatography, the hydrogen iodide being removed by an Amberlite section at the entrance to the column. Three determinations of the quantum yields of iso- and normal propyl iodide were made at 4790 Å. and two at 5125 Å. The results are summarized in Table I.

Within the accuracy of the experiments the quantum yields of each of the propyl iodides are the same above the convergence limit as below the convergence limit. This seems to indicate that the mechanism by which iodine reacts with the hydrocarbons is one involving thermalized iodine
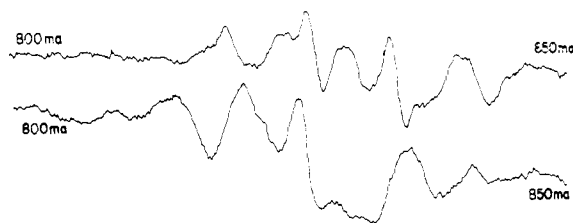

Fig. 4.—Electron spin resonance spectra: upper spectrum, $4 \times 10^{-3} M$ I_2 in $(C_2H_5)_2O$ in quartz sample tube irradiated at 77° K. in Pyrex Dewar with AH6 arc; lower spectrum, similar irradiation of I_2 in i-C_3H_7OH.

atoms since no other reactive iodine intermediate is formed by the absorption of light both above and below the convergence limit. Less than 1% of the iodine was consumed in the runs with the monochromator.

TABLE I

QUANTUM YIELDS OF PHOTOCHEMICAL REACTION OF IODINE WITH PROPANE

(1.2 mm. I_2, 125 mm. C_3H_8, 49°)

	4790 Å.	5125 Å.
ϕ (i-C_3H_7I)	$2.5 \pm 1.3 \times 10^{-4}$	$2.1 \pm 0.1 \times 10^{-4}$
ϕ (n-C_3H_7I)	$2.1 \pm 1.1 \times 10^{-4}$	$2.2 \pm 0.6 \times 10^{-4}$
$\dfrac{(i\text{-}C_3H_7I)^a}{(n\text{-}C_3H_7I)}$	1.08 ± 0.29	0.95 ± 0.67

^{a} Ratio calculated from the experiments of this table, plus other experiments in which ϕ values were not obtained because actinometry was not done.

In a single experiment, similar to those of Table I, in which ethane was substituted for propane the quantum yield of ethyl iodide was 1.2×10^{-4} which is about one fourth of the combined yields of normal and isopropyl iodides in the propane experiments.
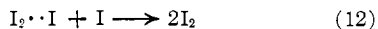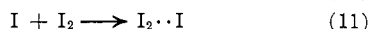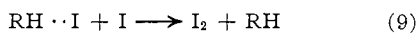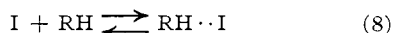
Discussion

Bleaching of I_2 in Glasses at Liquid Air Temperatures.—The fact that liquid solutions of I_2 in EPA, ethanol, ethyl ether or isopentane at room temperature can be bleached by doses of visible radiation similar to the exposure required for bleaching in the gla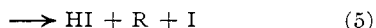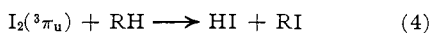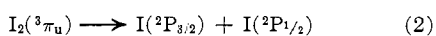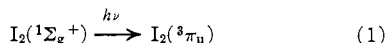ssy state at liquid air temperatures indicates that trapped iodine atoms are not required to explain the bleaching in the glass. Such trapping could not occur in the liquid phase. The appearance of the triiodide spectrum in the irradiated glass is positive indication that photochemical reaction of iodine with the solvent occurs at −185°. As noted above, the reappearance of color when bleached glasses are warmed to room temperature may be attributed to two causes. In those experiments where the irradiation dose is sufficient to convert most of the iodine to HI, slow reappearance of color appears to occur as a result of oxidation of the HI by a difficultly removable impurity. In those experiments where some HI is formed but unreacted I_2 remains, rapid appearance of color due to triiodide formation, as a result of greater ease of diffusion of I_2 and HI at the higher temperature, or as a result of a shift in the equilibrium constant, can account for the observation.

The formation of triiodide in $10^{-4} M$ I_2 solutions in the glass at liquid air temperatures indicates

that HI and I_2 can undergo appreciable diffusion at these temperatures (if it is correct to assume that the I_2 is monomolecularly dispersed).

Mechanism of Photochemical Reaction of Iodine with Carbon–Hydrogen Bonds.—The abstraction of hydrogen from hydrocarbons by ground state iodine atoms $(I + RH \rightarrow R + HI)$ has a low probability since the process is endothermic by some 20–30 kcal./mole. This is borne out by the report[9] that intense illumination with visible light produces no reaction between I_2 and CH_4 and by the fact that the reports of several investigators[10] of the photochemistry of iodine in liquid straight chain hydrocarbons give no evidence of the formation of HI.

It may be estimated[11] that the maximum possible quantum yield for propyl iodide formation in the experiments of Table I would be 8×10^{-11} if reaction were dependent on thermal iodine atoms abstracting hydrogen from C_3H_8 with an activation energy just equal to the endothermicity of the reaction (23 kcal./mole) and a probability factor of unity. Consequently, it must be concluded that the observed reaction, which has a quantum yield of 10^{-4}, involves either utilization of the energy supplied by the photon in excess of that required to dissociate the I_2 or that there is a possible mechanism involving concerted attack by two iodine atoms. The several possibilities which must be considered are listed below.

$$I_2(^1\Sigma_g^+) \xrightarrow{h\nu} I_2(^3\pi_u) \tag{1}$$

$$I_2(^3\pi_u) \longrightarrow I(^2P_{3/2}) + I(^2P_{1/2}) \tag{2}$$

$$\longrightarrow 2I(^2P_{3/2}) \tag{3}$$

$$I_2(^3\pi_u) + RH \longrightarrow HI + RI \tag{4}$$

$$\longrightarrow HI + R + I \tag{5}$$

$$I(^2P_{1/2}) + RH \longrightarrow HI + R \tag{6}$$

$$I(^2P_{3/2}) + RH \longrightarrow HI + R \tag{7}$$

$$I + RH \rightleftarrows RH \cdot \cdot I \tag{8}$$

$$RH \cdot \cdot I + I \longrightarrow I_2 + RH \tag{9}$$

$$\longrightarrow HI + RI \tag{10}$$

$$I + I_2 \longrightarrow I_2 \cdot \cdot I \tag{11}$$

$$I_2 \cdot \cdot I + I \longrightarrow 2I_2 \tag{12}$$
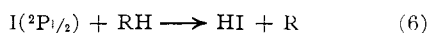
(9) J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

(10) See for example, (a) S. Aditya and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2680 (1957). (b) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 659 (1953). (c) J. Zimmerman and R. M. Noyes, *ibid.*, **18**, 658 (1958).

(11) By equating the rate of production of iodine atoms (*i.e.*, twice the rate of absorption of photons, which is 4×10^{18} photons per sec. per 50 cc. at 4790 Å.) to the rate of recombination $(= k_{C_3H_8}[I]^2[C_3H_8] + k_{I_2}[I]^2[I_2])$ the steady state concentration of atoms in the iodine propane systems studied may be estimated as 3×10^{-9} molar. For this purpose, $k_{C_3H_8}$ is taken as about[12a,b] $4 \times 10^9 1.^2$ mole^{-2} sec.$^{-1}$ and k_{I_2} as about[12c,d] $2 \times 10^{12} 1.^2$ mole^{-2} sec.$^{-1}$. At this steady state concentration, iodine atoms will undergo about 2×10^{17} collisions with propane molecules per cc. per sec. $(4\pi\sigma_1\sigma_2 n_1 n_2)$ of which the fraction $e^{-E/RT}$ or a total of 60 will lead to reaction in the optimum case where the probability factor is unity. Thus the maximum quantum yield for $E = 23$ kcal./mole is $60/8 \times 10^{11} = 8 \times 10^{-11}$.

(12) (a) K. E. Russell and J. Simons, *Proc. Roy. Soc.* (London), **A217**, 271 (1953). (b) R. L. Strong, J. C. W. Chien, P. E. Graf and J. E. Willard, *J. Chem. Phys.*, **26**, 1287 (1957). (c) M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (London), **A231**, 446 (1955). (d) D. L. Bunker and N. R. Davidson, *J. Am. Chem. Soc.*, **80**, 5085 (1958).

The iodine species produced in the gas phase experiments are shown in steps 1–3 and depend on the wave length of the exciting radiation. Step 2 takes place at wave lengths below the convergence limit, while step 3 occurs at wave lengths above the convergence limit as a result of collision induced predissociation. The fact that the quantum yields for product formation are the same above and below the convergence limit indicates that steps 4–6 cannot play an important part in the reaction mechanism. Step 7 is excluded because, as discussed above,[11] it cannot account for the observed quantum yield. Moreover, as a thermal reaction, it should favor the formation of isopropyl iodide over normal propyl iodide, whereas in fact, equal amounts are formed.

The sequence of reaction steps 8–10 is capable of accounting for the observed gas phase reactions. Steps 8 and 9, in which $RH \cdot \cdot I$ is a short lived collision complex, represent the most commonly accepted mechanism of three body recombination of halogen atoms in the gas phase.[12d] The gas phase reaction observed in the present work can be accounted for if one out of every 400 or so collisions between an iodine atom and an iodine atom-propane complex, which lead to stable products, yields not an iodine molecule but hydrogen iodide and the alkyl iodide. If this is the mechanism, the ratio of iodine atoms which undergo reaction 10 to those which re-form I_2 is 4×10^{-4} (Table I); that is, reaction 10 occurs once for every 2.5×10^3 times I_2 is formed by reactions 9 and 12. The rate constant of 12 $(R = k_{12}[I_2][I]^2)$ is known to be several hundred times greater than that of 9 $(R = k_{RH}[RH][I]^2)$, but is not known exactly.[12c,d] If the ratio is 500, then $1/6$ of the recombination events in our system (1.2 mm. I_2 and 125 mm. of C_3H_8) occurred by reaction 9 and $5/6$ by reaction 12. Reaction 10 is strongly exothermic. Consequently energy considerations do not require preferential formation of i-C_3H_7I relative to n-C_3H_7I, as required for reaction 7. Moreover, no wave length dependence is expected from this mechanism since the electronically excited $^2P_{1/2}$ atoms produced in step 2 and the $^2P_{3/2}$ atoms produced with excess kinetic energy in step 3 are rapidly reduced to the ground state and thermalized and usually have many different hydrocarbon partners before step 10 takes place. The lower quantum yield in ethane than propane, and still lower yield in methane[9] appears to indicate different branching ratios between recombination and reaction for the different compounds.

In the gas phase, the physical processes which accompany absorption of light by iodine are well understood as a function of the wave length of the absorbed light relative to the position of the band head. In solution in oxygenated solvents the absorption maximum is shifted from 5200 Å., which is characteristic of the gas phase, to about 4500 Å. If it is assumed that the difference in equilibrium internuclear separation between the ground and first excited electronic states is the same in solution as in the gas phase, then the convergence limit still lies some 200 Å. below the absorption maximum. If it is also assumed that this additional energy required for the convergence limit in solu-

tion in excess of that of the 4995 Å. quantum of the convergence limit in the gas phase is dissipated in overcoming charge-transfer bond strengths and solvation energies, the iodine species may be produced in solution by reactions 1–3 in nearly the same manner as in the gas phase except for the energy of the quanta required.

The electronic excitation energy of a $^2P_{1/2}$ iodine atom is 21.8 kcal./mole and at wave lengths just above the convergence limit the energy of an I_2-($^3\pi_u$) molecule in excess of the bond strength is only slightly less than this. The bond strength of the alpha carbon–hydrogen bond in ethyl alcohol can be computed from heats of formation[13] to be 92 kcal./mole. The bond strengths of the secondary C–H bonds in ethyl ether and isopentane are probably close to this value. Using this value, the heats of reaction of steps 4 to 7 are, respectively, −45.7, −0.7, −0.7 and 21 kcal./mole. Step 7 can be eliminated because of its endothermicity. The probability of the occurrence of steps 4 and 5 will be dependent upon their frequency factors relative to that for collision induced predissociation. Step 6 may take place if the electronic energy of the $^2P_{1/2}$ atom can be used very efficiently. It seems likely, however, that most of the observed reaction takes place through steps 8–10, particularly in view of the recent observation[14] by flash photolysis techniques of transient absorption spectra attributed to charge transfer complexes between iodine atoms and ethanol, ethyl ether and isopentane. In the condensed phase, process 10 may often involve iodine atoms from the same I_2 molecule, which have not escaped from the parent cage after having absorbed a photon. With thermalized atoms the process is some 23 kcal./mole exothermic. In solution the distinction between process 4 and process 10 becomes less distinct than in the gas phase. In addition to this type of process, mechanisms 5 or 6 must occur to a certain extent in the rigid glassy state at 77°K. in order to account for the observed free radical yield. It may represent only a small fraction of the total chemical reaction in the glass.

It has been demonstrated earlier that gaseous I_2 activated by 1849 Å. light in methane, ethane or hydrogen attacks the C–H and H–H bonds as an excited iodine molecule,[15] the yield depending on the pressure of the reactant since the reaction is in competition with fluorescence of the excited iodine molecule. The mechanism seems to be distinctly different from that of the reaction initiated by visible light. An attack of iodine atoms

on i-propyl iodide to produce HI, C_3H_6 and I has been postulated to explain the results obtained in a study of the photolysis of i-C_3H_7I.[16] Still other mechanisms of attack on hydrocarbons are available to iodine atoms which have been activated by the $I^{127}(n,\gamma)I^{128}$ process.[9,17] These are able to displace either H atoms or organic radicals from the hydrocarbon chain.

Free Radicals Produced by the Photochemical Reaction of Iodine in the Glassy State.—Exposure of ethanol in the glassy state at 77°K. to ionizing radiation produces trapped radicals which give a five line electron spin resonance pattern.[18] This is the pattern to be expected from four equally coupled protons and has the expected relative intensities 1:4:6:4:1. It has been attributed to the radical CH_3CHOH. Experiments with deuteriated alcohols[18c] have shown that there is no interaction with the hydroxyl proton.

The possibility of unequal coupling to the alpha and beta protons exists, and this could lead to eight lines. Such a pattern has been observed by Fujimoto and Ingram[19] during a study of radicals produced by photolysis of hydrogen peroxide in ethanol at 77°K. On warming to 90°K., these authors observed that a five line pattern was formed. Our spectra for radicals produced by the photochemical reaction of iodine with ethanol at 77°K. contain eight lines. On standing for 2 days at 77°K. they show a change from the eight line to a five line pattern analogous to the change reported by Fujimoto and Ingram to occur on warming from 77° to 90°K. It appears that in both cases the radical is CH_3CHOH. We have also observed an eight line pattern from ethyl ether and the radical responsible may be $CH_3CHOC_2H_5$. Abstraction of the secondary hydrogen from 2-propanol to give $(CH_3)_2COH$ would be expected to give a seven line pattern due to six equally coupled protons, as observed (Fig. 4).

It appears that the radicals are formed by loss of a secondary hydrogen by reaction 5 or 6. On standing for two days at 77°K., a reorientation seems to take place which equalizes the coupling of the unpaired electron to all the available protons.

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