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PHOTOLYSIS OF DIPHENYLIODONIUM SALTS IN ALCOHOL SOLUTIONS

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A complex mixture of products is produced when a diphenyliodonium salt is subjected to photochemical decomposition in alcohol solution. For example, photolysis of diphenyliodonium fluoroborate in isopropyl alcohol solution in a quartz tube for two hours at 71°, light 90% of the intensity of which has a wavelength of 2537 Å being used, gives benzene (87%), acetone (81%), iodobenzene (98%), biphenyl (2%), phenyl isopropyl ether (0.08%) and Bronsted acids (1.7 equivalents[1] of protons per mole of diphenyliodonium salt). These and data of several additional reactions are presented in Table 1. The fact that formation of benzene is inhibited by the presence of oxygen, iodine or 1,1-diphenylethylene indicates that a photochemically initiated chain reaction is operative. On the basis of these observations, and also on the basis of the observation (see Table 2) that similar products are produced by peroxide initiated decomposition reactions of diphenyliodonium salts in alcohol solutions,[2] we propose that the major reaction pathway is that shown in the accompanying Reaction Scheme. The key intermediate, a phenyliodinium cation radical, is similar to the diphenylsulfinium cation radical, which was shown to play an important role in the photodecomposition of triphenylsulfonium salts.[3,4] Furthermore, Miller and Hoffman[5] have presented evidence that aryliodinium cation radicals are formed in the electrochemical oxidation of organic iodides.

A mechanism in which a solvated electron is formed as a reactive species can be ruled out as a major pathway leading to products, inasmuch as the presence of known scavengers of the solvated electron, such as nitrate ion, acetone and Bronsted acids, have no marked effect on the yields and ratios of products (see Table 1).[3] Also, a photochemical heterolytic dissociation of the C-I bond to give a phenyl cation plus iodobenzene can be ruled out on the basis of the previously mentioned fact that the presence of radical scavengers, such as iodine, oxygen and 1,1-diphenylethylene,[6,7] was found to inhibit the formation of the major products containing the phenyl group, and this would not have been the case if the phenyl cation had been the precursor of these products. In addition, the yield of phenyl alkyl ether was distinctly minor in every experiment, and such an ether would be the major product if a phenyl cation were generated in an alcohol solution.

An electron transfer mechanism, shown below, for the initiation step of the chain reaction should increase in importance as the ease with which the counter anion can give up an electron to the associated acceptor cation is increased; however, there is no marked difference in the yields and ratios of products obtained from the diphenyliodonium fluoroborate, nitrate and chloride salts. Thus, the electron transfer mechanism does not appear to be as reasonable a possibility for the initiation step as the one shown in the Reaction Scheme.

$$(C_6H_5)_2\overset{+}{I} + X^- \rightleftharpoons (C_6H_5)_2I\text{-}X \xrightarrow{h\nu}$$

$$[(C_6H_5)_2I\cdot,X\cdot] \longrightarrow (C_6H_5)_2I\cdot + X\cdot$$

$$\downarrow$$

$$C_6H_5\cdot + C_6H_5I$$

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Table 1

The Irradiation of $Ph_2I^+X^-$ in ROH in a Quartz Tube

X^-	R	% Yield Products								
		Acetone	PhH	PhOR	PhCl	PhI	Ph-Ph	H^+	$Ph_2I^+X^-$	Atmosphere
BF_4^-	i-Pr	81	87	0.08	---	98	2.0	168	0.0	Argon[a]
"	"	51	48	0.16	---	85	2.0	128	12	Oxygen
"	Et	---	86	0.11	---	95	2.0	180	---	Argon
"	"	---	48	0.28	---	89	2.0	132	---	Oxygen
NO_3^-	"	---	89	0.05	---	96	2.0	92	---	Argon
"	"	---	61	0.10	---	91	2.0	84	---	Oxygen
"	"	---	86	trace	---	93	1.0	91	---	Argon[a]
"	"	---	0.0	0.40	---	39	0.05	---	80	Argon[b]
Cl^-	"	---	85	trace	1.1	95	1.0	86	---	Argon
"	"	---	77	0.43	1.6	91	1.0	83	---	Oxygen
"	"	---	4.7	0.21	8.2	38	0.0	---	47	Argon[c]

[a] -- 5.0×10^{-4} mole of $Ph_2I^+X^-$ in 2.0 ml. ROH irradiated in a Rayonet photochemical reactor at 71° for 2 hr. for the first six exp.; then 3.5×10^{-4} mole salt used in remaining experiments.

[b] -- 3.5×10^{-4} mole iodine added to reaction mixture

[c] -- 3.5×10^{-4} mole 1,1-diphenylethylene added to reaction mixture

Table 2

Peroxide Initiated Reactions of Diphenyliodonium Fluoroborate with Alcohols[a]

Peroxide	Alcohol	% Yield Products					
		Acetone	PhH	PhOR	PhI	Ph-Ph	H^+
Benzoyl Peroxide[b]	EtOH	---	81	trace	78	2.1	84[c]
" " [b]	i-PrOH	107	89	"	90	2.1	96[c]
" " [d]	"	84	73	"	73	1.2	76[c]
Hydrogen Peroxide[e]	"	27	15	none	15	trace	40

[a] -- All solutions contained 5.0×10^{-4} mole $Ph_2I^+\ BF_4^-$ and reactions were carried out at 71° for 90 min.

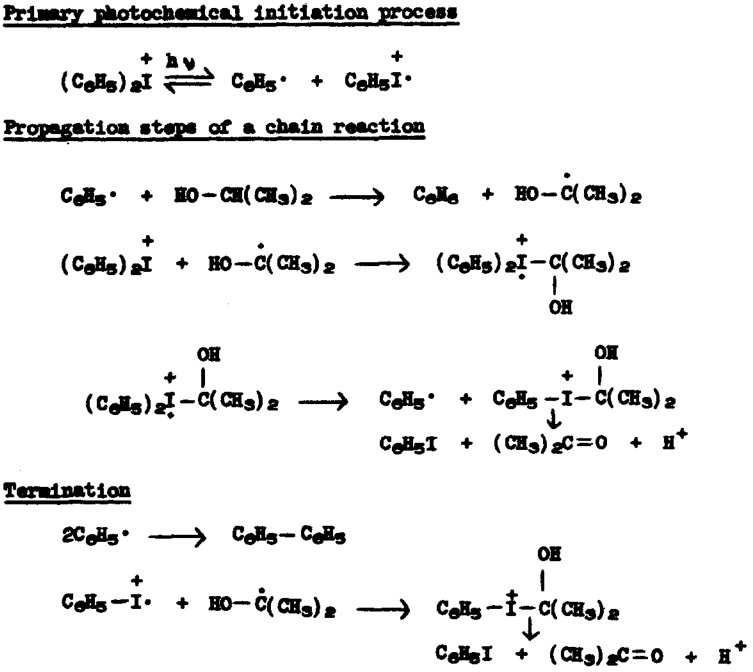
[b] -- 2.5×10^{-4} mole

[c] -- Corrected for benzoic acid produced

[d] -- 1.0×10^{-4} mole

[e] -- 9.0×10^{-5} mole

Reaction Scheme



Primary photochemical initiation process

$$(C_6H_5)_2\overset{+}{I} \overset{h\nu}{\rightleftharpoons} C_6H_5\cdot + C_6H_5\overset{+}{I}\cdot$$

Propagation steps of a chain reaction

$$C_6H_5\cdot + HO-CH(CH_3)_2 \longrightarrow C_6H_6 + HO-\dot{C}(CH_3)_2$$

$$(C_6H_5)_2\overset{+}{I} + HO-\dot{C}(CH_3)_2 \longrightarrow (C_6H_5)_2\overset{+}{\underset{\cdot}{I}}-\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2$$

$$(C_6H_5)_2\overset{+}{\underset{\cdot}{I}}-\overset{OH}{\overset{|}{C}}(CH_3)_2 \longrightarrow C_6H_5\cdot + C_6H_5-\overset{+}{I}-\overset{OH}{\overset{|}{C}}(CH_3)_2 \downarrow C_6H_5I + (CH_3)_2C{=}O + H^+$$

Termination

$$2C_6H_5\cdot \longrightarrow C_6H_5-C_6H_5$$

$$C_6H_5-\overset{+}{I}\cdot + HO-\dot{C}(CH_3)_2 \longrightarrow C_6H_5-\overset{+}{\dot{I}}-\overset{OH}{\overset{|}{C}}(CH_3)_2 \downarrow C_6H_5I + (CH_3)_2C{=}O + H^+$$