STUDY OF THE PHOTOCHEMICAL REACTION BETWEEN TRIPHENYLPHOSPHINE AND DIPHENYLIODONIUM BOROFLUORIDE

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Abstract

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STUDY OF THE PHOTOCHEMICAL REACTION BETWEEN TRIPHENYLPHOSPHINE AND DIPHENYLIODONIUM BOROFLUORIDE

Only one paper has been devoted to the photochemical decomposition of diaryliodonium salts. Irving and Reid (^{1}) investigated the action of ultraviolet light on iodides, bromides, chlorides, and borofluorides of diphenyl- and di-(*n*-fluorophenyl)-iodonium in chloroform, benzene, hexane, CCl_4, and ether. They showed that diphenyl- and di-(*n*-fluorophenyl)-iodonium iodides decompose under the action of daylight or ultraviolet light at a considerable rate. In the case of decomposition of $(C_6H_5)_2JJ$ in chloroform under the action of ultraviolet light, the reaction products are benzene and iodobenzene. At the same time, these authors note that the bromides, chlorides, and borofluorides of the diaryliodonium salts investigated by them practically do not decompose under the action of ultraviolet light.

We have shown (^{2}) that diphenyliodonium chloride or borofluoride is capable of entering into a photochemical reaction with triphenylphosphine, with arylation of the latter taking place. The reactions occurring may be represented by the following general equation:

$$(C_6H_5)_3P + (C_6H_5)_2JX \xrightarrow[C_2H_5OH]{h\nu} (C_6H_5)_4PX + C_6H_5J,$$

where $X = Cl, BF_4$.

The present work is devoted to the study of the mechanism of this reaction. We found that the reaction between triphenylphosphine and diphenyliodonium borofluoride under irradiation with a PRK-4 mercury lamp proceeds at practically the same rate in both quartz and glass test tubes. This indicates that the photochemical reaction studied by us is affected by visible light*.

Table 1

Yield of $(C_6H_5)_4PBF_4$ in various solvents upon irradiation with a PRK-4 mercury lamp

Solvent	Ratio $(C_6H_5)_3P$: $(C_6H_5)_2JBF_4$	Reaction duration, h	Yield of $(C_6H_5)_4PBF_4$, %
CH_3CH_2OH	1 : 1	15	52.7
$CH_3CH_2CH_2OH$	1 : 1	12	60
CH_3COCH_3	1 : 1	6	85.5
CH_3COCH_3	2 : 1	4	85
CH_3COCH_3	4 : 1	6	88

We further established that triphenylphosphine reacts successfully with diphenyliodonium borofluoride under irradiation with an incandescent lamp**, in diffuse daylight, and especially rapidly in bright sunlight.

As the solvent for the reaction studied by us we used, in addition to ethyl alcohol, propyl alcohol and acetone. The latter is the most convenient solvent, since in it, unlike in alcohols, the starting substances are readily soluble. In addition, when carrying out the reacci in acetone the yield of tetraphenylphosphonium borofluoride is higher than in alcohol (85.5% versus 60%), as is seen from the data in Table 1.

The ratio of reagents has practically no effect on the yield of $(C_6H_5)_4PBF_4$. Thus, if the reaction is carried out in acetone under illumination with a PRK-4 mercury lamp and with a reagent ratio $(C_6H_5)_3P : (C_6H_5)_2JBF_4$ equal to 4 : 1, the yield of $(C_6H_5)_4PBF_4$ is 88%, whereas in the case of equimolecular amounts of the reagents it is 85.5% (see Table 1).

Table 2

Results of photochemical reactions between triphenylphosphine and $(C_6H_5)_2JBF_4$ under illumination with a PRK-4 mercury lamp

No.	$(C_6H_5)_3P$, amount in g	$(C_6H_5)_2JBF_4$, amount in g	Inhibitor, mol. %	Solvent, ml	Reaction time, h	Yield, %
1	0,325	0,460	–	C_2H_5OH 20	15	52,7
2	0,325	0,460	Hydroquinone 21	C_2H_5OH 20	15	54
3	0,325	0,460	Hydroquinone 140	C_2H_5OH 10	12	24,5

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* Glass is capable of transmitting light no shorter than 330–340 mμ.

** For the reaction to proceed successfully, incandescent lamps with a power of at least 150 W are suitable; in this case the distance between the reaction test tube and the lamp should not exceed 10 cm.

No.	$(C_6H_5)_3P$, amount in g	$(C_6H_5)_2JBF_4$, amount in g	Inhibitor, mol. %	Solvent, ml	Reaction time, h	Yield, %
4	0,262	0,368	*m*-Dinitrobenzene 240	C_2H_5OH 10	6	30
5	0,16	0,23	–	C_3H_7OH 10	12	60
6	0,16	0,23	Hydroquinone 38	C_3H_7OH 10	12	60
7	0,13	0,184	Hydroquinone 200	C_3H_7OH 5	7	30
8	0,52	0,74	–	CH_3COCH_3 10	6	85,5
9	0,262	0,368	*m*-Dinitrobenzene 6	CH_3COCH_3 10	6	71
10	0,262	0,368	Hydroquinone 10	CH_3COCH_3 10	5	70,0
11	0,262	0,368	Hydroquinone 300	CH_3COCH_3 10	5	18

A substantial influence on the photochemical reaction between triphenylphosphine and diphenyliodonium borofluoride is exerted by such substances as hydroquinone and *m*-dinitrobenzene, i.e., inhibitors of radical reactions. For example, if the reaction is carried out in scattered light in *n*-propyl alcohol or acetone, then upon addition of 10 mol.% hydroquinone, tetraphenylphosphonium borofluoride is not formed at all. At the same time, the same amounts of hydroquinone, when the reaction is carried out in acetone in bright sunlight, have no effect on it. If the reaction is conducted under illumination with a PRK-4 mercury lamp, inhibitors act differently depending on the solvent used. The results of these experiments are given in Table 2.

As is seen from the data in this table, when the reaction is carried out in ethyl or *n*-propyl alcohol, the addition of 20-38 mol.% hydroquinone (experiments Nos. 2 and 6) does not affect the yield of tetraphenylphosphonium borofluoride. At the same time, the use of large amounts of hydroquinone or *m*-dinitrobenzene (experiments Nos. 3, 4, 7) leads to a sharp decrease in the yield (from 60% to 24-30%) of $(C_6H_5)_4PBF_4$. In the case where acetone is used as the solvent, the photochemical reaction proves to be still more sensitive to the action of inhibitors. Thus, addition of 10 mol.% hydroquinone to the reaction mixture lowers the yield of tetraphenylphosphonium borofluoride from 85 to 70%, and in the presence of 300 mol.% hydroquinone* $(C_6H_5)_4PBF_4$ is formed in only 18% yield. An analogous influence is exerted by *m*-dinitrobenzene.

It should be noted that, when the photochemical reaction is carried out both in acetone and in alcohols, addition of *m*-dinitrobenzene or hydroquinone leads only to a decrease in the yield of tetraphenylphosphonium borofluoride; the starting diaryliodonium salt, $(C_6H_5)_2JBF_4$, in all experiments presented in Table 2, decomposes completely. At the same time, we have established that diphenyliodonium borofluoride itself does not decompose under the action of light under the experimental conditions.

* Blank experiments showed that $(C_6H_5)_2JBF_4$ does not react with hydroquinone.

In those cases where the photochemical reaction between triphenylphosphine and diphenyliodonium borofluoride was carried out in alcohol,* benzene and an aldehyde were formed as by-products. The benzene was detected by us by means of the electronic absorption spectrum, and the aldehyde by reaction with fuchsinsulfurous acid. These substances apparently could have been formed only as a result of radical decomposition of the diphenyliodonium salt and interaction of the diphenyliodonium** (or the phenyl radical formed from it) radical with the solvent:

$$(C_6H_5)_2J\cdot + CH_3CH_2OH \to C_6H_6 + C_6H_5J + CH_3\dot{C}HOH.$$

The radical $CH_3\dot{C}HOH$ formed is then converted into the aldehyde. Until recently it was generally accepted that diphenyliodonium borofluoride, on interaction with nucleophilic reagents, is capable of decomposing only heterolytically (^{3}). However, recently two of us, together with G. G. Lyatiev (^{4}), showed that in the reaction of $(C_6H_5)_2JBF_4$ with aliphatic amines of the type $(C_2H_5)_2NH$ or $(C_2H_5)_3N$, the iodonium salt decomposes homolytically:

$$(C_6H_5)_2JBF_4 + :N(C_2H_5)_3 \longrightarrow [(C_6H_5)_2J \cdots N(C_2H_5)_3]^+BF_4^- \longrightarrow$$

$$\longrightarrow (C_6H_5)_2J\cdot + (C_2H_5)_3\dot{N}^+ + BF_4^-.$$

The data obtained in the present work, as it seems to us, also testify in favor of radical decomposition of the diphenyliodonium salt. At first $(C_6H_5)_3P$ reacts with $(C_6H_5)_2JBF_4$ with formation of a complex of the type $[(C_6H_5)_2J : P(C_6H_5)_3]^+BF_4^-$, which then decomposes homolytically under the action of light:

$$[(C_6H_5)_2J \cdots P(C_6H_5)_3]^+BF_4^- \xrightarrow{h\nu} (C_6H_5)_2J\cdot + \dot{P}^+(C_6H_5)_3 + BF_4^-$$

The above complex, in contrast to a complex of the type $[(C_6H_5)_2J : NH_2C_6H_5]^+BF_4^-$, was not obtained by us in the free state. However, the results obtained in studying the UV absorption spectrum indicate the formation of such a complex. When acetone solutions of $(C_6H_5)_3P$ and $(C_6H_5)_2JBF_4$ are mixed, a new band appears in the UV absorption spectrum, with a maximum at 336 mμ. Triphenylphosphine has a maximum at 255 mμ, and diphenyliodonium borofluoride at 225 mμ and a shoulder at about 258 mμ. The reaction products have maxima up to 280 mμ. Thus, the appearance in an acetone solution of a mixture of $(C_6H_5)_3P$ and $(C_6H_5)_2JBF_4$ of a band with a maximum at 336 mμ is due to the formation of some new substance. In our opinion, this substance is the complex $[(C_6H_5)_2J : P(C_6H_5)_3]^+BF_4^-$. Such an assumption is based on the fact that the known complex $[(C_6H_5)_2J : NH_2C_6H_5]^+BF_4^-$ (^{4}) has a maximum at 329 mμ, as was shown by us and G. G. Lyatiev. A certain displacement of the maxima is quite natural, since in one case there is a J—N bond, and in the other a J—P bond.

On the basis of the foregoing, we assume that the photochemical reaction between $(C_6H_5)_3P$ and $(C_6H_5)_2JBF_4$ has a chain radical character and proceeds according to the following scheme:

$$(C_6H_5)_2JBF_4 + :P(C_6H_5)_3 \rightarrow [(C_6H_5)_2J : P(C_6H_5)_3]^+BF_4^-$$

* When the reaction was carried out in acetone, benzene was not sought.

** It is possible that the diphenyliodonium radical immediately decomposes into iodobenzene and a phenyl radical.

$$[(C_6H_5)_2J \cdots P(C_6H_5)_3]^+BF_4^- \xrightarrow{h\nu} (C_6H_5)_2J\cdot + {}^+P(C_6H_5)_3 + BF_4^- \qquad \text{(I)}$$

$$(C_6H_5)_2J\cdot + :P(C_6H_5)_3 \rightarrow (C_6H_5)_4P\cdot + C_6H_5J \qquad \text{(II)}$$

$$(C_6H_5)_4P\cdot + (C_6H_5)_2J^+BF_4^- \rightarrow (C_6H_5)_4P^+BF_4^- + (C_6H_5)_2J\cdot \qquad \text{(III)}$$

etc.

The ion-radical $(C_6H_5)_3P^+\cdot$ formed in the course of the reaction is either oxidized by atmospheric oxygen, giving $(C_6H_5)_3PO$*, or reacts with the solvent, abstracting hydrogen from the latter:

$$(C_6H_5)_3P^+\cdot + CH_3CH_2OH \rightarrow (C_6H_5)_3P^+H + CH_3\dot{C}HOH \qquad \text{(IV)}$$

and oxidizing the alcohol to aldehyde, which was detected by us. As for the triphenylphosphonium cation, it must be very unstable (triphenylphosphine is a very weak base) and readily (practically instantaneously) lose a proton**, regenerating $(C_6H_5)_3P$: $(C_6H_5)_3P^+H \rightarrow (C_6H_5)_3P + H^+$. As is evident from the scheme, the radical $(C_6H_5)_2J\cdot$ plays an important role in propagation of the chain (reaction III) and in the formation of $(C_6H_5)_4PBF_4$. Its interaction with inhibitors of radical reactions leads to chain termination. The longer the chain, the smaller the amounts of inhibitors needed to stop the reaction. It is known that in photochemical reactions the chain becomes shorter with increasing light intensity, since the chain length is inversely proportional to the square root of the light intensity (5). Therefore, when the reaction is carried out in scattered light, rather small amounts of inhibitors are sufficient to suppress the reaction. At the same time, when the reaction mixture is irradiated with a PRK-4 mercury lamp, large amounts of hydroquinone or *m*-dinitrobenzene are required to suppress the reaction of formation of $(C_6H_5)_4PBF_4$.

The radical $(C_6H_5)_2J\cdot$, in addition to triphenylphosphine (reaction II), can probably also react with the solvent, as a result of which a by-product—benzene—should be formed:

$$(C_6H_5)_2J\cdot + R:H \rightarrow C_6H_5 + C_6H_5J + R\cdot \qquad \text{(V)}$$

Obviously, the more readily reaction (V) proceeds in comparison with reaction (II), the more extensively there will occur, so to speak, "useless" decomposition of the diphenyliodonium salt, i.e., decomposition not leading to the formation of $(C_6H_5)_4PBF_4$, and the lower the yield of tetraphenylphosphonium borofluoride will be. Apparently, the diphenyliodonium radical $(C_6H_5)_2J\cdot$ reacts with inhibitors analogously to reaction (V). This, probably, explains the fact that the addition of hydroquinone or *m*-9-dinitrobenzene to the reaction mixture leads only to a decrease in the yield of $(C_6H_5)_4PBF_4$, but practically does not affect the amount of decomposed iodonium salt—$(C_6H_5)_2JBF_4$.

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* We established that in the photochemical reaction between $(C_6H_5)_3P$ and $(C_6H_5)_2JBF_4$, $(C_6H_5)_3PO$ is obtained as a by-product in an amount of 6–9%.

** We showed that the reaction medium after carrying out the reaction is acidic.

*** This reaction should also lead to chain termination.

Note: Figure translations are in progress. See original paper for figures.

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