# On the Reactions of Diphenyliodonium and Triphenylsulphonium Salts with Hydroxyl and 2-Hydroxy-2-Propyl Radicals

## Evidence for Reduction of Diphenyliodonium Ions to Diphenyliodo Radicals

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Hydroxyl radicals react with diphenyliodonium ions, $Ph_2I^+$, and triphenylsulphonium ions, $Ph_3S^+$, in aqueous solution at room temperature with rate constants $\geq 5 \times 10^9$ l/mol s. These reactions lead to the formation of a broad transient absorption band with a maximum at ca. 370 nm, which is attributed to OH-adducts with cyclohexadienyl structures. 2-Hydroxy-2-propyl radicals react with diphenyliodonium ions in aqueous solution at room temperature with $k_3 = 6 \times 10^7$ l/mol s. The transient absorption band formed in this reaction has a maximum at about 390 nm and is attributed to diphenyliodo radicals, $Ph_2I^{\cdot}$. In contrast, no detectable reaction occurred with 2-hydroxy-2-propyl radical and triphenylsulphonium ion.

## 1. Introduction

Carbon-centered free radicals produced photochemically or thermally can be oxidized to carbocations by onium salts [1]. This reaction has been utilized to initiate the polymerization of tetrahydrofuran, epoxides and other compounds, that undergo cationic polymerization. Iodonium salts such as diphenyliodonium hexafluoroarsenate, $Ph_2IAsF_6$, and the corresponding phosphate, $Ph_2IPF_6$, have been successfully employed as oxidizing agents [2]. Typical reactions, postulated for the generation of cationic initiators by irradiation of benzophenone in the presence of propanol-2 and $Ph_2IAsF_6$, are:

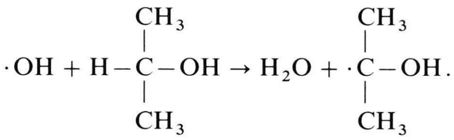
$$Ph_2CO + (CH_3)_2CHOH \xrightarrow{h\nu} Ph_2\dot{C}-OH + (CH_3)_2\dot{C}-OH\,, \tag{1}$$

$$Ph_2\dot{C}-OH + Ph_2I^+ \longrightarrow (Ph)_2\overset{+}{C}-OH + Ph_2I^{\cdot}\,, \tag{2}$$

$$(CH_3)_2\dot{C}-OH + Ph_2I^+ \longrightarrow (CH_3)_2\overset{+}{C}-OH + Ph_2I^{\cdot}\,. \tag{3}$$

It is seen that the reduction of diphenyliodonium ion leads to diphenyliodo radical, $Ph_2I^{\cdot}$. However, the absorption spectrum of $Ph_2I^{\cdot}$ seems to be unknown, which has limited the interpretation of flash photolysis studies in which diphenyliodonium salts take part [3].

In the present work diphenyliodo radicals were produced in the absence of potential overlapping chromophores such as benzophenone ketyl radical, in order to facilitate the determination of its absorption spectrum. For this purpose 2-hydroxy-2-propyl radicals were generated by reacting ·OH radicals with propanol-2 in the presence of $Ph_2I^+$:



$$\cdot OH + H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH \rightarrow H_2O + \cdot\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH\,. \tag{4}$$

Reaction (4) occurs with $k = 4 \times 10^9$ l/mol s. Hydroxyl radicals were generated by the radiolysis of $N_2O$-saturated water. Pulse radiolysis in conjunction with optical absorption detection was employed: dilute aqueous solutions containing both propanol-2 and $Ph_2IPF_6$ were irradiated with single 50 ns pulses of 16 MeV electrons generated by a linear accelerator. Complementary studies with $Ph_3SBF_4$ were also performed.

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## Results

Pulse radiolysis of $N_2O$-saturated solutions of $Ph_2IPF_6$ ($4.0 \times 10^{-3} - 1.5 \times 10^{-2}$ mol/l) in the absence of propanol-2 resulted in the formation of the transient absorption spectrum (a) shown in Figure 1. This spectrum, which is attributed to the product of the reaction of $\cdot OH$ radicals with diphenyliodonium ions, was formed during the pulse, i.e. with a lifetime < 50 ns. When the solution contained 1.1 mol/l propanol-2, almost all (ca. 98%) of the $\cdot OH$ radicals were scavenged by the alcohol according to reaction (4). In this case only a small portion of the transient absorption was formed during the pulse. The major portion was formed after the pulse. The absorption spectrum corresponding to the slow mode of formation is shown in Figure 2. It possesses a maximum at about 390 nm. The rate of formation of this spectrum increased with increasing diphenyliodonium salt concentration and conformed with 1st order kinetics. Figure 3 shows a plot of the 1st order rate constant vs. the diphenyliodonium salt concentration. From the slope of the straight line one obtains $k = 6.0 \times 10^7$ l/mol s.

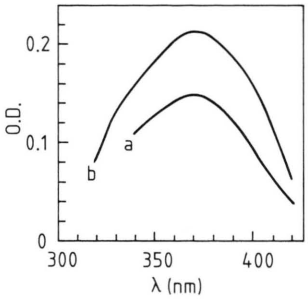


Fig. 1. Irradiation of $Ph_2IPF_6$ ($4 \times 10^{-3}$ mol/l) (a) and $Ph_3SBF_4$ ($3 \times 10^{-3}$ mol/l) (b) in $N_2O$-saturated aqueous solution with a 50 ns pulse of 16 MeV electrons at room temperature. $D_{abs} = 60$ Gy. Transient absorption spectra formed during the pulse.

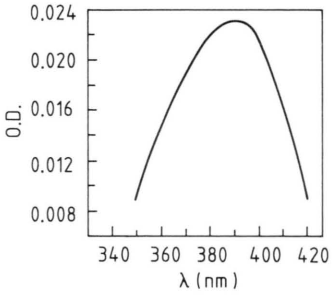


Fig. 2. Irradiation of an $N_2O$-saturated aqueous solution containing $Ph_2IPF_6$ ($4 \times 10^{-3}$ mol/l) and propanol-2 (1.12 mol/l). The spectrum presented here was obtained from the difference in the optical densities recorded at 10 and 1 μs after the end of the pulse. $D_{abs} = 60$ Gy.

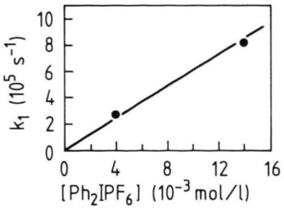
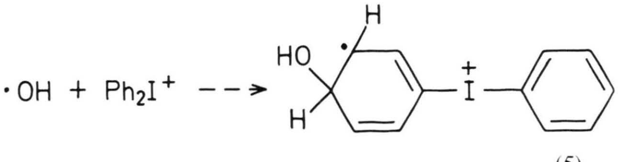


Fig. 3. Reaction of 2-hydroxy-2-propyl radicals with $Ph_2I^+$ ions. Plot of the pseudo-1st order rate constant vs. the iodonium salt concentration. For other conditions refer to legend to Figure 2.

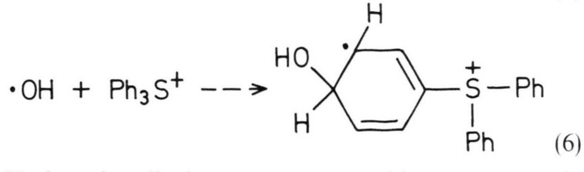
When triphenylsulphonium tetrafluoroborate was exposed to the attack of $\cdot OH$ radicals in $N_2O$-saturated aqueous solutions at concentrations between $1.2 \times 10^{-3}$ and $1.2 \times 10^{-2}$ mol/l, the transient absorption spectrum (b) in Fig. 1 with a broad maximum at 370 nm was formed during the pulse. However, upon irradiating solutions of $Ph_3SBF_4$ containing 1.12 mol/l propanol-2, an additional absorption was not formed after the pulse as in the case of diphenyl iodonium salt solutions. With $Ph_3SBF_4$ solutions, only a very weak absorption formed during the pulse corresponding to the depletion of $\cdot OH$ radicals by reaction with propanol-2.

## Discussion

The spectra shown in Fig. 1 (a) and (b) are attributed to the products of the reaction of the hydroxyl radical with $Ph_2I^+$ and $Ph_3S^+$, respectively. These products are presumably the adducts formed according to the reactions.



(5)



(6)

Hydroxyl radicals are prone to add to compounds containing aromatic rings whereas they frequently abstract hydrogens from aliphatic compounds. Hydroxyl adducts with cyclohexadienyl structure are reported to possess absorption maxima at ca. 320 nm [4].

Taking into account a possible red-shift of the maximum due to substitution of a hydrogen by iodine or sulphur, it seems justified to assign the spectra in Fig. 1 to the adducts formed according to reactions (5) and (6), respectively. The rapid build-up of the products of the reaction of $\cdot$OH radicals with $Ph_2I^+$ and $Ph_3S^+$, respectively, during the pulse ($\tau \leq 50$ ns) indicates high bimolecular rate constant in both cases: $k_2 \geq 5 \times 10^9$ l/mol s.

The addition of propanol-2 to the solution at a sufficiently high concentration resulted in suppression of the OH adduct formation. In the case of $Ph_2IPF_6$, a new transient absorption was formed relatively slowly after the pulse. These results are interpreted in support of reaction (3), and the new absorption is attributed to $Ph_2I^{\cdot}$ radicals. It follows that the measured rate constant, $k = 6.0 \times 10^7$ l/mol s, applies to reaction (3). In this connection it is interesting to note that a similar value, $k = 3.0 \times 10^7$ l/mol s was reported by Timpe [5] for the reaction of benzophenone ketyl radicals, $Ph_2\dot{C}OH$, with $Ph_2I^+$ ions. The slightly higher value found in our case might be due to a higher electron density at the radical site in the 2-hydroxy-2-propyl radicals.

A different situation was encountered in the case of the triphenylsulphonium salt. Whereas $Ph_3S^+$ ions behaved similarly to $Ph_2I^+$ ions in the reaction with hydroxyl radicals, a significant difference in the reactivity of these ions towards 2-hydroxy-2-propyl radicals was found. In contrast to $Ph_2I^+$ ions reaction of $Ph_3S^+$ ions with 2-hydroxy-2-propyl radicals was not detected.

This finding is in accordance with the finding that triphenylsulphonium salts are not capable of initiating free radical promoted cationic polymerization [6, 7], which was explained in terms of the quite different redox potentials (relative to SCE) of the two ions: $-1.2$ V ($Ph_3S^+$) [8] and $-0.2$ V ($Ph_2I^+$) [9]. Similarly, Baumann et al. [10] were unable to detect a reaction of benzophenone ketyl radicals with triphenylsulphonium ions in flash photolysis and spin trapping experiments.

## Experimental Part

### Materials

Propanol-2 (E. Merck, pro analysis) was distilled prior to use. Diphenyliodonium hexafluorophosphate and triphenylsulphonium tetrafluoroborate were prepared as previously described [11].

### Irradiations

The solutions were irradiated with 16 MeV electrons in rectangular quartz cells after bubbling with $N_2O$ for 30 minutes. Fast electrons were generated by a linear accelerator (Vickers, L-band type). The absorbed dose was determined with the aid of the Fricke dosimeter employing $O_2$-saturated $Fe^{2+}$ solutions ($G(Fe^{3+}) = 13.0$).

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