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The Catalytic Role of Iodide Ion / Iodine Couple in the Photo-Reduction of 10-Methylacridinium Ion with Diphenylphosphine Oxide

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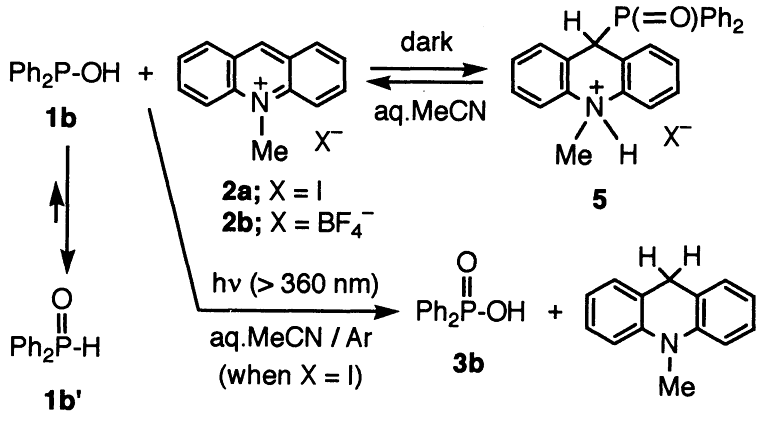
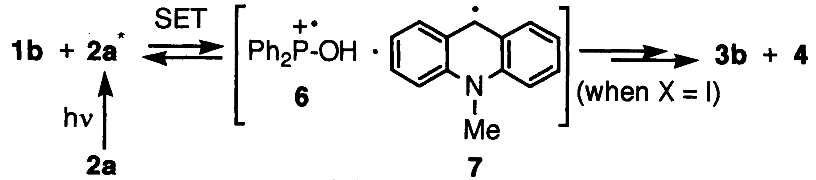
Photo-redox between diphenylphosphine oxide and 10-methylacridinium iodide with visible light in aqueous acetonitrile under argon atmosphere is initiated by single electron transfer from the phosphorus compound to the acridinium salt in the photo-excited state giving diphenylphosphinic acid and 10-methylacridan as the final products. Iodide ion/iodine couple plays a crucial role for transferring an electron in this reaction.

While isopropyl diphenylphosphinite (**1a**) undergoes the Arbuzov-type reaction with 10-methylacridinium iodide (**2a**) in aqueous acetonitrile in the dark,[1,2] the reaction under photo-excitation with visible light gives rise to single electron transfer (SET) from the former to the latter to yield isopropyl diphenylphosphinate (**3a**) and 10-methylacridan (**4**) as the final products.[2] Interestingly, iodide ion or iodine is required for this photo-reaction to take place, and the catalysis by iodide ion/iodine couple in transferring an electron has tentatively been postulated.[2] Recently, we found that diphenylphosphine oxide (**1b'**), which may tautomerize to diphenylphosphinous acid (**1b**) upon the reaction,[3] similarly reacts with **2a** in aqueous acetonitrile under the irradiation to give the corresponding oxidation products, diphenylphosphinic acid (**3b**), and **4**. We then examined the role of iodide ion and iodine in this photo-redox reaction mainly based on the product analysis and obtained clear evidence to support the previous postulation.

Upon mixing the solutions of diphenylphosphine oxide (**1b'**) and **2a** in acetonitrile[4] in equimolar amounts (1.25×10^{-2} M) in the dark, an ammonium adduct **5** was formed immediately. The adduct **5** was in the equilibrium with the starting materials. Presumably the reaction proceeds through tautomerization of **1b'** to a trivalent form **1b** followed by the Arbuzov-type process (Scheme 1).[5] When the same solution of **1b'** and **2a** was subjected to irradiation with visible light from a Xe-lamp (> 360 nm with a glass filter) under argon atmosphere for 60 min, the formation of **3b** as well as **4**, instead of **5**, was recognized on HPLC (Entry 1 in Table 1). The products were identified based on the comparisons of the retention times and UV spectra obtained on HPLC equipped with a photodiode array UV-vis detector with those of the authentic samples. The yields of the products were determined on HPLC. No reduction product **4** was obtained in the photo-reaction under the aerobic conditions (Entry 6 in Table 1). Photolysis of **1b** without **2a** did not give **3b** even under the aerobic conditions (Entry 7 in Table 1). The acridinium salt **2a** was stable under the irradiation in the absence of **1b**. Furthermore, spectrophotometric analyses showed that neither **1b'** nor **5** absorbs the light but only **2a** is photo-



Scheme 1

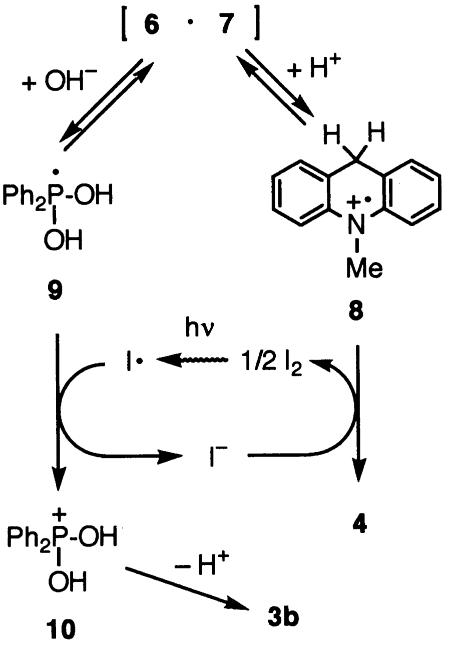


Scheme 2.

excited under these photochemical conditions. These findings indicate that the initial step of this photo-process is SET from **1b** to **2a** in the photo-excited state, **2a***, as has been well established for the similar photo-reduction of **2a** by **1a**$^{2)}$ or triphenylphosphine.$^{6)}$ During this step, the cation radical **6** and 10-methyl-dihydroacridinyl radical (**7**) are generated from **1b** and **2a**, respectively,$^{7)}$ which are eventually converted to **3b** and **4**, respectively (Scheme 2). The reduction potential E^{o}_{red} of **2*** has been reported to be 2.3 V vs. SCE,$^{8)}$ and the oxidation potential of **1b** is estimated to be lower than this value based on a reported value E^{o}_{ox} = 1.40 V vs SCE for triphenylphosphine;$^{9)}$ that is, the SET may be exothermic. Examination with time-course revealed that the ammonium adduct **5** is formed even under the irradiation but disappears gradually as **3b** and **4** are accumulated. Since **5** is transparent at the wave-lengths longer than 360 nm, the possibility that photo-decomposition of **5** leads to the products is ruled out. Evidently **5** disappears through dissociation to the starting materials.

The dihydroacridinyl radical **7** can be protonated to form the cation radical **8** to some extent under the conditions,$^{10)}$ and **8**, if once formed, would be reduced to **4** by iodide ion present in the system as a counter anion of the acridinium cation (Scheme 3). This might be the case judging from the reported values of redox potentials, E^{o}(**8**/**4**) = 0.80$^{11)}$ and $E^{o}(I_2/2I^-)$ = 0.290 V$^{12)}$ vs. SCE. Examinations with ^{1}H NMR and GC-MS on the reaction mixture in acetonitrile containing D_2O (0.5% v/v) confirmed that one of hydrogens at 9-position in **4** is introduced from water as expected.$^{13)}$ The reaction sequence proposed here is further supported by the fact that the reaction without iodide ion gives neither **3b** nor **4** in any amounts with only producing **5** thermally (Entry 2 in Table 1). In addition, no products except for **5** was obtained in the reaction of **1b'** with **2b** (X = BF_4) in the presence of tetrabutylammonium bromide as expected from higher redox potential for $Br_2/2Br^-$ (0.819 V vs SCE)$^{12)}$ than for **8**/**4** (Entry 4 in Table 1). The effect of iodide ion on the yields of the products is indeed apparent in the reactions of **1b'** with **2a** (X = I) or **2b** (X = BF_4) in the presence of various amounts of tetrabutylammonium iodide, in which the yield of **4** increases with increasing the total amount of iodide ion (closed triangles in Fig. 1). Noticeably, that no photo-reaction products were obtained in the absence of iodide ion also manifests that the initial SET is reversible (Scheme 2).

The cation radical **6**, on the other hand, can interact with a water molecule present in the system to give a phosphoranyl radical **9**. Iodine generated from iodide ion in the reduction of **8** dissociates to iodine radical under the irradiation,$^{14)}$ and a reported value of the redox potential $E^{o}(I\bullet/I^-)$ = 0.95 V vs. SCE$^{15)}$ is certainly high enough so that iodine radical oxidizes **9** to a phosphonium ion **10**; a half-wave reduction potential for tetraphenyl-



Scheme 3.

phosphonium salt $E_{1/2} = -1.68$ V vs. SCE has been reported.[16] Thus, the oxidation of **9** to **10** by an iodine radical, during which an iodide ion is regenerated, followed by the elimination of proton from **10** in the Arbuzov fashion produces **3b**.[17]

It is now obvious that iodide ion/iodine couple contributes to the oxidation and the reduction of equimolar amounts of **8** and **9**, respectively, as represented in Scheme 3. The addition of iodine, in place of iodide ion, to the solution of **1b'** and **2b** ($X = BF_4$) under the irradiation also brings about the formation of **3b** and **4** (Entry 5 in Table 1), which strongly supports the occurrence of the catalytic cycle composed of iodide ion and iodine. It seems likely that the reduction of **8** to **4** is coupled to the oxidation of iodide ion to iodine, not to iodine radical, in this catalytic cycle,

Table 1. Photo-Reaction of **1b'** with **2**[a)]

Entry	Atmos-phere	X in **2**	Addi-tive	Yield/ %[b)] **1b'**[c)]	**3b**	**4**	**5**[d)]
1	Ar	I	–	0	100	59	0
2	Ar	BF_4^-	–	67	0	0	33
3	Ar	BF_4^-	I^- e)	16	75	46	3
4	Ar	BF_4^-	Br^- f)	36	0	0	57
5	Ar	BF_4^-	I_2 g)	7	93	52	0
6	air	I	–	0	57	0	14
7	air	– h)	–	97	0	0	0
8	Ar i)	I	–	52	0	0	48

a) Xenon-lamp; > 360 nm with a Toshiba glass filter L-39, $[\mathbf{1b'}]_0 = [\mathbf{2}]_0 = 1.25 \times 10^{-2}$ M in aq.MeCN, for 60 min. b) Determined on HPLC based on $[\mathbf{1b'}]_0$. c) Recovered. d) Detected as **11** on HPLC; see Ref. 5. e) Tetrabutylammonium iodide (1.0 eq.). f) Tetrabutylammonium bromide (1.0 eq.). g) 1.0 eq. as iodine radical. h) In the absence of **2**. i) In the dark.

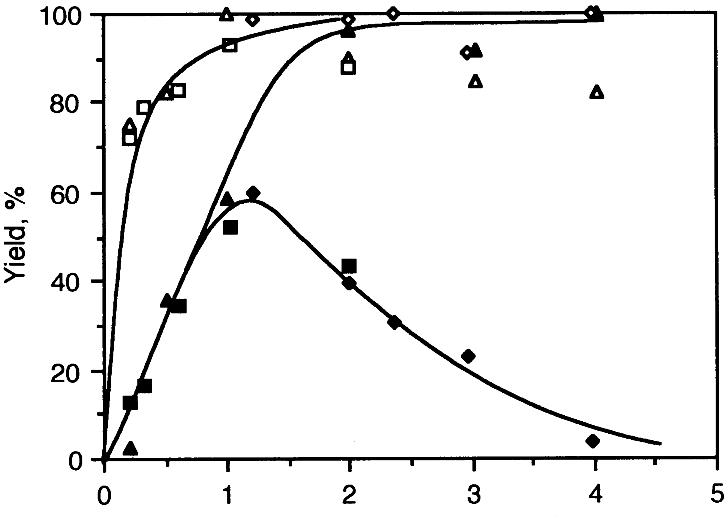


Fig. 1. Plot of the yields of **3b** and **4** against the ratio of the total amount of I^- and/or I• equivalent to the initial amount of **1b'**. For the reactions of **1b'** with **2a** (X = I) in the presence of tetrabutylammonium iodide (△ and ▲), with **2b** ($X = BF_4^-$) in the presence of iodine (□ and ■), and with **2a** (X = I) in the presence of iodine (◇ and ◆). Open and closed symbols represent the yields of **3b** and **4**, respectively.

since the redox potential for **8/4** is higher than that for $I_2/2I^-$ but lower than that for $I\bullet/I^-$.[18] Importantly, the dependence of the yields of the products on the initial amount of iodine (as an iodine atom equivalent) is essentially same as that observed for iodide ion when the initial amount of iodine-atom equivalent is smaller than that of **1b'** (closed squares in Fig. 1).

An excess amount of iodine lowers the yield of **4**. Control experiment showed that this is mainly due to thermal oxidation of **4** by iodine to the starting material **2**.[19] This reaction may be operative as well when the amount of iodine is smaller, which partly accounts for the discrepancy in the yields of **3b** and **4**. In addition, iodine-mediated thermal oxidation of **1b'** to **3b** as well as photo-decomposition of **4** in the presence of iodide ion was observed. These side reactions altogether make it quite difficult to establish the precise stoichiometry for the present redox reaction. Efforts are being made in order to elucidate quantitative aspects of the mechanism.

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4) Acetonitrile was distilled on calcium hydride prior to the use. The water content of this solvent was estimated to be *ca.* 0.1% by the Karl-Fischer method. The addition of 0.5% of water to the solvent resulted in no substantial difference in the results.
5) Because **5** is deprotonated to the conjugate base, (9,10-dihydro-10-methyl-9-acridinyl)diphenylphosphine oxide, **11**, during HPLC analysis in which H_2O/MeOH (20/80 (v/v)) is used as the eluent, **5** was experimentally detected as **11** on HPLC. The formation of **5** was confirmed by ^1H NMR spectroscopy; signals from the reaction mixture in CD_3CN were different from those of **11** but were identical to those observed when **11** was treated with *p*-toluenesulfonic acid in CD_3CN. Comparison of ^{31}P NMR chemical shift (δ from H_3PO_4 34 ppm) observed from the reaction mixture with that of **11** (δ 27 ppm in $CDCl_3$) also supports the structure **5**. The formation of **5** was observed under either the deaerated or the aerobic conditions.
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18) Alternatively, highly exothermic reaction between I• and **9** to produce I^- and **10** in this catalytic cycle may make it possible that this cycle is composed of I^- and I•.
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