

## PHOTOLYTIC DECOMPOSITION OF THE PERIODITE ION IN AQUEOUS SOLUTION

M. SADIQ SUBHANI AND RIZWANA LATIF

Department of Chemistry, Quaid-i-Azam University, Islamabad

(Received January 23, 1991; revised August 10, 1992)

The photolytic decomposition of an aqueous solution of the periodate ion ( $\text{IO}_4^-$ ) at  $\text{pH } 6.6 \pm 0.2$  was studied using a 253.7nm wavelength for photolysis. The quantum yields  $\phi$  for the disappearance of  $\text{IO}_4^-$  and for the formation of products  $\text{IO}_3^-$  and  $\text{O}_2$  were determined experimentally in Argon saturated deaerated,  $\text{N}_2\text{O}$  saturated, and deaerated scavenger containing systems. The observed values are  $\phi(-\text{IO}_4^-) = 0.73 \pm 0.01$ ,  $\phi(\text{IO}_3^-) = 0.74 \pm 0.01$  and  $\phi(\text{O}_2) = 0.38 \pm 0.02$ .

**Key words:** Photolytic decomposition, Aqueous solution, Periodate ions.

### Introduction

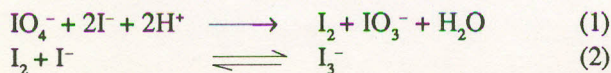
Various modes of photochemical decomposition of oxyanions in aqueous solutions have been reported in the literature [1-12]. In case of  $\text{IO}_4^-$  ion in aqueous system, some flash photolysis and pulse radiolysis studies were reported in the literature [13-16]. A complete mechanism for the photolytic decomposition was not available in the literature.

In the work presented here, investigations were carried out using 253.7nm light to determine the nature of the primary processes involved and the end products formed. Steady state photolysis studies were carried out for this purpose. These qualitative and quantitative studies helped us to suggest a mechanism for photolytic decomposition of periodate anion in aqueous solution at that wavelength.

### Experimental

All chemicals used were of A R grade supplied by Merck or B.D.H. Argon and  $\text{N}_2$  gases of high purity were supplied by Pakistan Oxygen Ltd. All solution were freshly prepared using triply distilled water just before the experiment. A quartz cell with 5 cm diameter and 2 cm thickness was used as reaction cell for the photochemical work. U1 G1-15 light source, supplied by UVP Inc., was used for obtaining UV light of 253.7 nm wavelength for irradiation. A double beam UV visible spectrophotometer Model Hitachi 220S was used during this work for all absorbance measurements.

**Analysis.** A known volume of an aliquot amount of  $\text{IO}_4^-$  and a definite volume of 0.5 M KI in 0.5  $\text{NaHCO}_3$  solution was added to a volumetric flask and mixed well. This produces a yellow colouring due to  $\text{I}_2$  and  $\text{I}_3^-$  ions produced by the reactions (1) and (2).



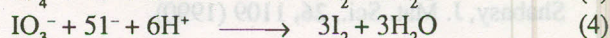
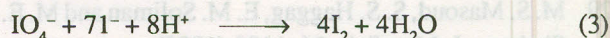
Under the described conditions the reaction between  $\text{IO}_3^-$

and  $\text{I}^-$  is almost stopped for all practical purposes.

The iodine liberated in reaction (1) was extracted with benzene. The absorbance due to  $\text{I}_2$  in benzene was measured at 297 nm. The molar absorption co-efficient  $\epsilon$  of  $\text{I}_2$  in benzene was determined experimentally using a solution of known iodine concentration in benzene. The value of  $\epsilon$  was found to be  $9.38 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 297 nm at  $25^\circ$ . The concentration of  $\text{IO}_4^-$  is determined from the measured concentration of  $\text{I}_2$  via equation (a).

$$[\text{I}_2] = [\text{IO}_4^-] \quad (a)$$

For the measurement of  $[\text{IO}_3^-]$  in photolysed solutions a known volume (same as above) was mixed with a known volume of 1M.  $\text{H}_2\text{SO}_4$  solution containing 0.5 M KI. The iodine thus produced by the following reactions (3) and (4)



was measured directly as  $\text{I}_3^-$  at 400 nm with absorption coefficient  $\epsilon = 5.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at  $25^\circ$ , determined experimentally using freshly prepared iodine solutions in presence of 1M KI. At this wavelength only  $\text{I}_3^-$  absorbs. Thus the concentration of  $\text{IO}_3^-$  was calculated by the relationship.

$$3[\text{IO}_3^-] = [\text{I}_2]_{\text{H}_2\text{SO}_4} - [\text{I}_2]_{\text{NaHCO}_3} \quad (5)$$

Gaseous products were analysed by gas chromatography.

**Actinometry.** A potassium ferrioxalate actinometer was used to measure the light intensity absorbed ( $I_a$ ) by the system [17-18]. A known volume of  $10^{-3}$  M solution of  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$  was irradiated for different intervals of time at a fixed position, using the same reaction cell, by light of 253.7 nm wavelength. The solution was analysed by forming complex with 1-10 phenanthroline and the absorbance due to the complex was measured at 510 nm with  $\epsilon = 1.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at that wavelength. From the concentration of  $\text{Fe}^{2+}$  ions produced

the quantum yield  $\phi_{Fe^{2+}}$  was found to be 1.25 at 253.7 nm the value of Ia was obtained as described in the literature [17,18].

**Results and Discussions**

Aqueous solutions  $10^{-3}$ – $5 \times 10^{-3}$  M  $IO_4^-$  anions at pH 6.6  $\pm 0.2$  were used throughout the experimental work at temperature  $25 \pm 1^\circ$ . These solutions were photolysed for different intervals of time (up to 4 min.) using 253.7 nm wavelength.

*Deaerated and Ar saturated system.* Deaerated aqueous solutions were photolysed and the yield/dose plots for the disappearance of  $IO_4^-$  ion and products ( $IO_3^-$  ion and  $O_2$ ) were found to be linear. (Figs. 1 and 2).

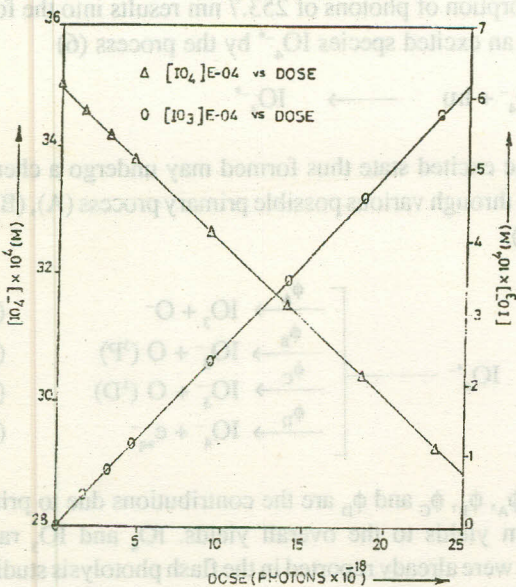


Fig. 1. Photolysis of  $2.8 \times 10^{-3}$  M  $IO_4^-$  ion in aqueous deaerated solution.  $\Delta$  = Disappearance of  $[IO_4^-]$  with dose (Ia),  $O$  = Formation of product  $IO_3^-$  ion with dose (Ia)

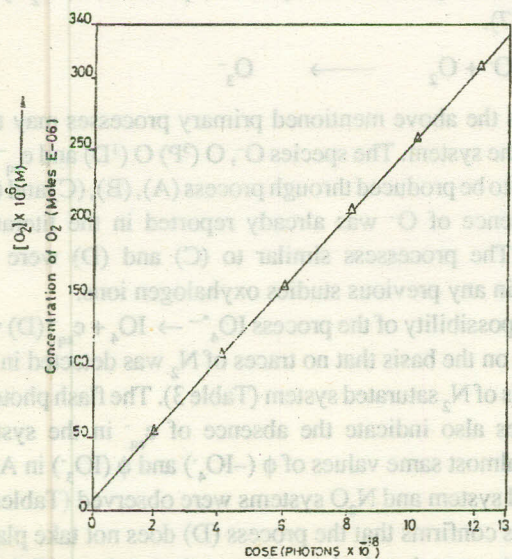


Fig. 2. Photolysis of  $IO_4^-$  ion in aqueous Ar saturated solution.  $[IO_4^-] = 10^{-3}$  M, Formation of  $O_2$  with dose.

The quantum yields calculated from the slopes of these plots by least square method are summarized in Table 1. In Argon saturated solution of  $IO_4^-$  ions the measured quantum yields are reported in Table 2.

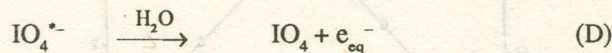
TABLE 1. DEAERATED SYSTEM.

$\phi (IO_4^-)$	$0.73 \pm 0.01$
$\phi (IO_3^-)$	$0.74 \pm 0.02$
$\phi (O_2)$	$0.38 \pm 0.02$

TABLE 2. Ar SATURATED SYSTEM.

$\phi (IO_4^-)$	$0.73 \pm 0.01$
$\phi (IO_3^-)$	$0.74 \pm 0.02$
$\phi (O_2)$	$0.74 \pm 0.02$

*N<sub>2</sub>O Saturated system.* Aqueous  $N_2O$  saturated solutions of  $10^{-3}$  M  $IO_4^-$  were photolysed to scavenge  $e_{aq}^-$  which may be produced in the primary process



The product yields for  $IO_3^-$  and for the disappearance of  $IO_4^-$  ( $-[IO_4^-]$ ) were plotted against dose (Ia) and fitting to straight lines was done by the least square method.

In these experiments no traces of  $N_2$  gas were detected. This indicates that the process (D) is not taking place under the condition employed as  $e_{aq}^-$  was expected to react with  $N_2O$  to give  $N_2$  and  $O$ .

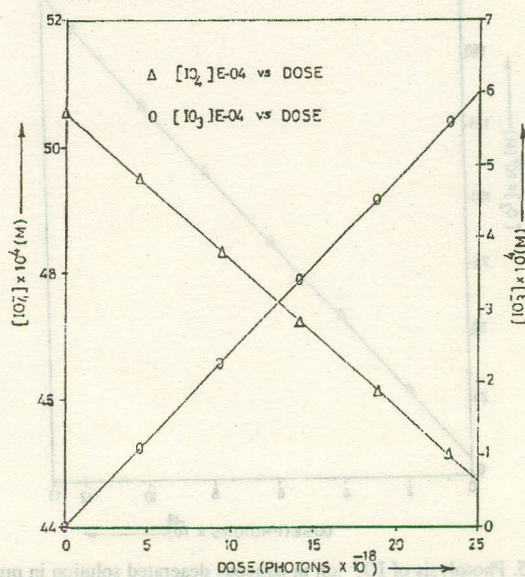
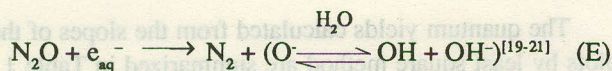


Fig. 3. Photolysis of  $2.8 \times 10^{-3}$  M  $IO_4^-$  ion in aqueous  $N_2O$  saturated.  $\Delta$  = Disappearance of  $IO_4^-$  with dose (Ia),  $O$  = Formation of product  $IO_3^-$  ion with dose (Ia).



The quantum yields obtained are summarized in Table 3.

*In presence of formiate ion.* The quantum yields  $\phi(-\text{IO}_4^-)$ ,  $\phi(\text{IO}_3^-)$  and  $\phi(\text{O}_2)$  were also measured on photolysis of aqueous solution of  $4.2 \times 10^{-3}$  M  $\text{IO}_4^-$  ion in presence of  $8 \times 10^{-2}$  M formiate ion at  $\text{pH } 6.6 \pm 0.2$ . Yield/dose plots were linear and the values of quantum yields obtained from the slopes of the plots are summarized in Table 4 (Figs. 4 and 5).

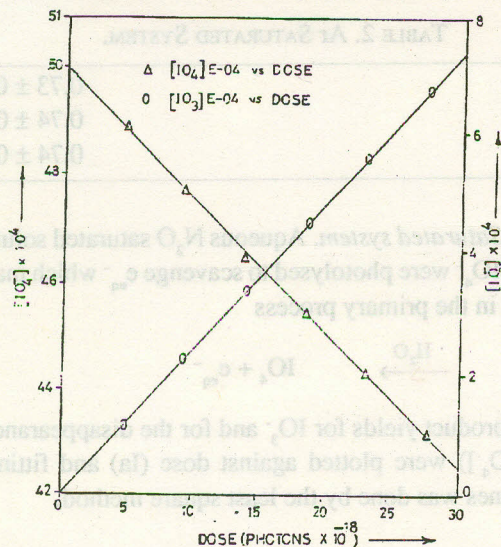


Fig. 4. Photolysis of  $\text{IO}_4^-$  ion in aqueous deaerated solution in presence of formiate ion.  $[\text{IO}_4^-] = 4.2 \times 10^{-3}$  M, and  $[\text{HCOO}^-] = 8 \times 10^{-2}$  M.  $\Delta$  = Disappearance of  $\text{IO}_4^-$  with dose (1a),  $\text{O}$  = Formation of product  $\text{IO}_3^-$  ion with dose (1a).

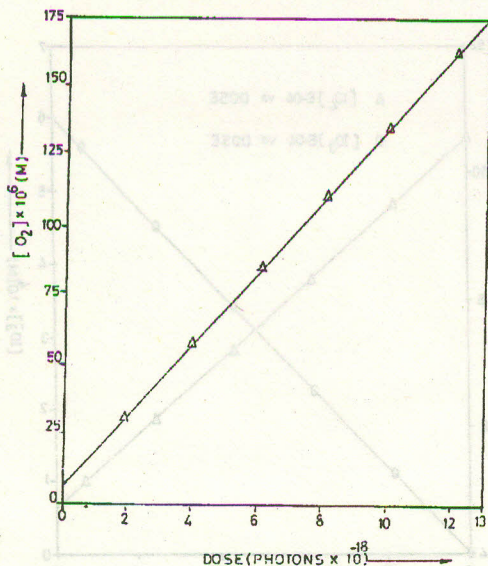


Fig. 5. Photolysis of  $\text{IO}_4^-$  ion in aqueous deaerated solution in presence of formiate ion.  $[\text{IO}_4^-] = 4.2 \times 10^{-3}$  M, and  $[\text{HCOO}^-] = 8 \times 10^{-2}$  M. Formation of product  $\text{O}_2$  with dose (1a).

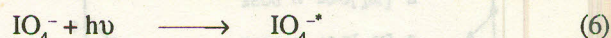
TABLE 3.  $\text{N}_2\text{O}$  SATURATED SYSTEM.

$\phi(\text{N}_2)$	Zero
$\phi(-\text{IO}_4^-)$	$0.71 \pm 0.01$
$\phi(\text{IO}_3^-)$	$0.72 \pm 0.01$

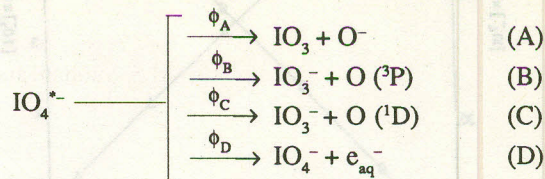
TABLE 4. DEAERATED SYSTEM IN PRESENCE OF FORMIATE ION.

$\phi(-\text{IO}_4^-)$	$0.73 \pm 0.02$
$\phi(\text{IO}_3^-)$	$0.72 \pm 0.02$
$\phi(\text{O}_2)$	$0.19 \pm 0.02$

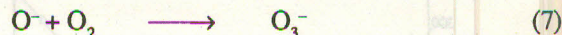
The periodate ion like other oxyhalogen [4,5,6(b),8] ions on absorption of photons of 253.7 nm results into the formation of an excited species  $\text{IO}_4^{*-}$  by the process (6)



The excited state thus formed may undergo a chemical change through various possible primary process (A), (B), (C) and (D).



where  $\phi_A$ ,  $\phi_B$ ,  $\phi_C$  and  $\phi_D$  are the contributions due to primary quantum yields to the overall yields.  $\text{IO}_4$  and  $\text{IO}_3$  radical species were already reported in the flash photolysis studies of  $\text{IO}_4^-$  and  $\text{IO}_3^-$  in aqueous solution [5, 13-16]. These species were reported to decay by second order kinetics. The species  $\text{O}_3^-$  was also reported in the system in presence of  $\text{O}_2$  by the process (7).



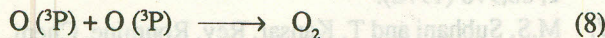
Thus the above mentioned primary processes may take place in the system. The species  $\text{O}^-$ ,  $\text{O} (^3\text{P})$ ,  $\text{O} (^1\text{D})$  and  $e_{\text{aq}}^-$  are expected to be produced through process (A), (B), (C) and (D). The presence of  $\text{O}^-$  was already reported in the literature [13,14]. The processes similar to (C) and (D) were not reported in any previous studies oxyhalogen ions.

The possibility of the process  $\text{IO}_4^{*-} \rightarrow \text{IO}_4^- + e_{\text{aq}}^-$  (D) was ruled out on the basis that no traces of  $\text{N}_2$  was detected in the photolysis of  $\text{N}_2$  saturated system (Table 3). The flash photolysis studies also indicate the absence of  $e_{\text{aq}}^-$  in the system because almost same values of  $\phi(-\text{IO}_4^-)$  and  $\phi(\text{IO}_3^-)$  in Ar or deaerated system and  $\text{N}_2\text{O}$  systems were observed (Tables 1-3). all this confirms that the process (D) does not take place.

Steady state photolysis results mentioned above (Table 1-4) obtained under different sets of conditions are useful in

establishing the probable primary processes and their relative contributions ( $\phi_A$ ,  $\phi_B$ ,  $\phi_C$  and  $\phi_D$ ) to the overall quantum yields.

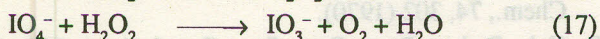
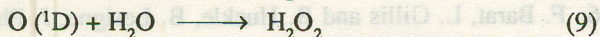
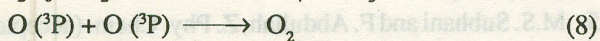
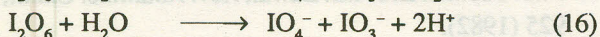
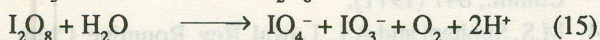
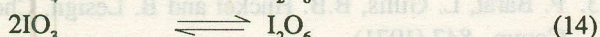
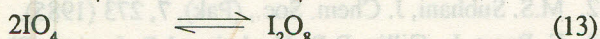
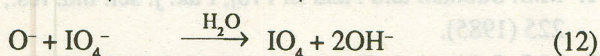
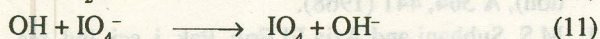
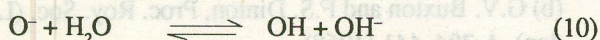
From these results, and other photolytic and radionlytic studies on oxyanions, and from the reaction of O ( $^3P$ )



and of O ( $^1D$ ) with water



reported in the literature [6(b,c), 22-24] the following secondary reactions are suggested for this system.



The processes (13) and (14) are similar to those suggested in the case of oxychlorine and oxybromine anions.

The above suggested mechanism predicts  $O_2$  and  $IO_3^-$  as the probable products. These are the only two products observed experimentally (Table 4). The processes (B), (C) (15), (16) and (17) lead to  $IO_3^-$  whereas (8), (15) and (17) lead the formation of  $O_2$ .

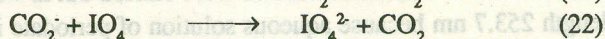
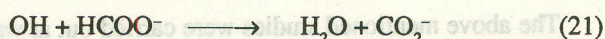
The value of  $\phi(-IO_4^-)$ ,  $\phi(IO_3^-)$  and  $\phi(O_2)$  give a good material balance in oxygen and iodine in the systems under consideration (Ar saturated, deaerated in presence of formiate ion). Thus no oxygen or iodine containing products are missing. Solutions were photolysed even at alkaline pH but no  $IO^-$  was detected. This further confirmed that  $O_2$  and  $IO_3^-$  are the only products formed. The expected  $\phi(-IO_4^-)$ ,  $\phi(IO_3^-)$  and  $\phi(O_2)$  can be expressed in terms of  $\phi_A$ ,  $\phi_B$  and  $\phi_C$  as

$$\phi(-IO_4^-) = \phi_A + \phi_B + 2\phi_C \quad (18)$$

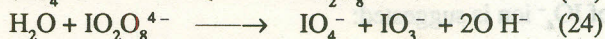
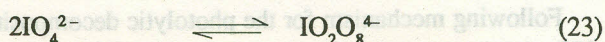
$$\phi(IO_3^-) = \phi_A + \phi_B + 2\phi_C \quad (19)$$

$$\phi(O_2) = 0.5 \phi_A + 0.5\phi_B + \phi_C \quad (20)$$

To evaluate the magnitude of  $\phi_A$ ,  $\phi_B$  and  $\phi_C$  for the processes (A), (B) and (C) scavenger for OH radical (formiate ion) was added to the system before photolysis. In presence of formiate ion reaction (11), (12), (13) and (15) are expected to be contributing insignificantly to  $\phi(O_2)$ ,  $\phi(-IO_4^-)$  and  $\phi(IO_3^-)$ . In deaerated solution in presence of formiate ion.



reactions (21) and (22) are most probably taking place similar to those reported for  $MnO_4^-$  system in the literature [25]. The species  $IO_4^{2-}$  has already been identified in the radiolysis work and reported to decay by second order kinetics [5, 13-16] reactions (23) and (24) are suggested



and are reported in the literature.

Thus  $\phi(O_2)$ ,  $\phi(-IO_3^-)$  and  $\phi(IO_4^-)$  can be written as (25), (19) and (18).

$$\phi(O_2) = 0.5 \phi_B + \phi_C \quad (25)$$

$$\phi(IO_3^-) = \phi_A + \phi_B + 2\phi_C \quad (19)$$

$$\phi(-IO_4^-) = \phi_A + \phi_B + 2\phi_C \quad (18)$$

Taking values of  $\phi(O_2)$ ,  $\phi(-IO_3^-)$  and  $\phi(IO_4^-)$  from Table 4 the value of  $\phi_A = 0.39 \pm 0.01$  and  $\phi_B + 2\phi_C = 0.38 \pm 0.01$  were obtained. It was not possible to calculate  $\phi_B$  and  $\phi_C$  separately from the experimental data available.

The values of  $\phi_A$  and  $\phi_B + 2\phi_C$  were used to predict the expected values for  $\phi(O_2)$ ,  $\phi(-IO_4^-)$ ,  $\phi(IO_3^-)$  for  $N_2O$ , Ar saturated and deaerated systems. The values obtained on calculations are found to be in good agreement with the observed results. (Tables 5-7).

TABLE 5. Ar SATURATED SYSTEM.

	Experimental	Calculation
$\phi(O_2)$	—	0.36
$\phi(-IO_4^-)$	$0.73 \pm 0.02$	0.73
$\phi(IO_3^-)$	$0.74 \pm 0.02$	0.73

TABLE 6. DEAERATED SYSTEM.

	Experimental	Calculation
$\phi(O_2)$	$0.73 \pm 0.02$	0.36
$\phi(-IO_4^-)$	$0.73 \pm 0.01$	0.73
$\phi(IO_3^-)$	$0.74 \pm 0.02$	0.73

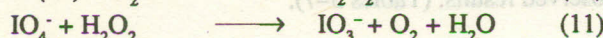
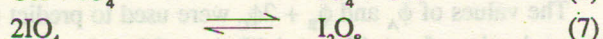
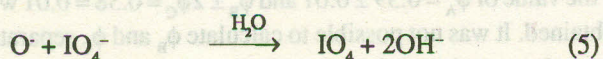
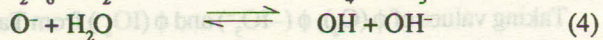
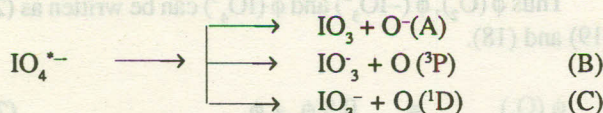
TABLE 7.  $N_2O$  SATURATED SYSTEM.

	Experimental	Calculation
$\phi(O_2)$	--	0.36
$\phi(IO_4^-)$	$0.71 \pm 0.01$	0.73
$\phi(IO_3^-)$	$0.72 \pm 0.01$	0.73

The above mentioned studies were carried out at wavelength 253.7 nm because aqueous solution of periodate ions was found to have negligible absorbance at wavelength greater than 300 nm. Thus, it was not possible to see the wavelength dependence of primary quantum yields,  $\phi_A$ ,  $\phi_B$  and  $\phi_C$  for the system under consideration.

### Conclusion

Following mechanism for the photolytic decomposition of  $\text{IO}_4^-$  ion is suggested:



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Calculation	Experimental	$\phi(\text{O}_2)$
0.36	$0.73 \pm 0.02$	$\phi(\text{O}_2)$
0.73	$0.73 \pm 0.01$	$\phi(\text{IO}_4^-)$
0.73	$0.74 \pm 0.02$	$\phi(\text{IO}_3^-)$

Calculation	Experimental	$\phi(\text{O}_2)$
0.36	--	$\phi(\text{O}_2)$
0.73	$0.71 \pm 0.01$	$\phi(\text{IO}_4^-)$
0.73	$0.72 \pm 0.01$	$\phi(\text{IO}_3^-)$