

Flash-photolysis Study of Potassium Hydroxide Solutions†

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Flash-photolysis experiments of KOH solutions ($[\text{KOH}] > 0.03 \text{ M}$) are carried out in hydrogen- and air-saturated solutions; the formation of hydrated electrons is observed in hydrogen-saturated solutions, but the formation of $\text{O}_2^{\cdot-}$ and $\text{O}_3^{\cdot-}$ is observed in the presence of molecular oxygen and a reaction mechanism supported by kinetic computer simulations of the results is proposed.

The dissociation threshold energy of water, yielding H^{\cdot} atoms and HO^{\cdot} radicals, lies in the region 6.41–6.71 eV.¹ Accordingly, photodissociation of water [eqn. (1a)]² has been reported to occur with quantum efficiencies of the order of 0.3 at 184.9 nm, 0.7 at 147.9 nm, and approaching 1 at 123.6 nm.

In addition to eqn. (1a), the photolytic formation of e^-_{aq} from eqn. (1b) has already been demonstrated in flash-photolysis experiments for photons of 6.54 eV.⁶ Experiments using the formation of fluoride ions from SF_6 as a specific monitor for e^-_{aq} indicate that photolysis of water in the wavelength range 175–200 nm produces hydrated electrons with a constant quantum yield of 0.05 ± 0.01 at pH 4–9,^{3,4} increasing slowly with the irradiation energy.⁵ The observed independence of the quantum yields on pH was suggested as an indication that water, but not HO^- , is a source of e^-_{aq} . An increase in the quantum yield above pH 9 was reported to be due to the reaction between H^{\cdot} and HO^- yielding e^-_{aq} [eqn. (10)]. However, photoionization of OH^- , eqn. (2), has been proposed as the main reaction in H_2 -saturated KOH solutions.³

Photolysis of alkaline H_2 -saturated solutions has been reported as a nearly ideal source of e^-_{aq} , since the reactions [eqns. (15) and (10)] add to the yields of hydrated electron produced from eqns. (1) and (2). However, no studies have been reported on the photolysis kinetics in oxygen- or air-saturated KOH solutions. Here we report the results of our flash-photolysis studies in the presence of dissolved oxygen, which turned out to be a rather clean method of ozonide radical generation.

Experimental

KOH (Mallinckrodt) was used without further purification. Distilled water was passed through a Millipore system and deaerated in order to avoid dissolution of carbon dioxide. Flash-photolysis experiments were carried out in a conventional apparatus (Xenon Co. model 720C) with modified optics and electronics.⁷ For observation wavelengths higher than 600 nm, a 500 nm cut-off filter was placed in front of the monochromator in order to eliminate detection of harmonics.

In those experiments where detection above 650 nm was necessary, high analysing lamp intensities were required due to the low sensitivity of the photomultiplier (PMT) at these wavelengths. Under these conditions, detection at lower wavelengths (higher PMT sensitivity) required amplification values almost below the limit of the recommended range of linear responsivity of the PMT. This may be the cause of the discrepancy between our spectrum and that reported, both of which are shown in Fig. 1.

In order to detect the formation of hydrated electrons, aqueous solutions of KOH (pH > 12.5) degassed by three freeze-pump-thaw cycles were saturated with almost 1 atm of H_2 and the cell was sealed. The solutions were irradiated for 10–20 min with a continuous mercury lamp, prior to the flash-photolysis experiments, in order to eliminate traces of oxygen and/or organic material.³ Photolysis studies of KOH in the presence of dissolved oxygen were performed in synthetic air-saturated solutions in order to avoid CO_2 dissolution. The presence of CO_3^{2-} in the solutions was

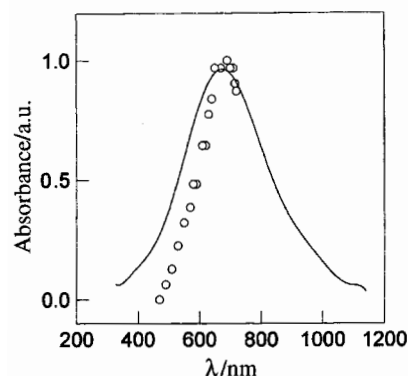


Fig. 1 Absorption spectrum of e^-_{aq} . Data taken from ref. 3 represented by — and experimental data obtained in this work represented by \circ (uncorrected spectrum, refer to text for details)

checked by flash irradiation experiments at 600 nm (λ_{max} of $\text{CO}_3^{\cdot-}$ absorption⁸).

Results and Discussion

The absorption traces observed immediately after pulsed irradiation of H_2 -saturated KOH solutions showed a decay lifetime of the order of 0.5 ms and an absorption spectrum with a maximum around 715 nm, Fig. 1. Both the absorption spectrum and the decay lifetime are in agreement with reported values for the hydrated electron,^{3,9} thus indicating hydrated electron formation under our experimental conditions.

On the other hand, the absorption traces observed after flash irradiation of KOH solutions saturated with synthetic air show a complex dependence on wavelength in the range 260–500 nm, indicating the absorption of more than one species. Fig. 2 shows the traces observed at 440 and 270 nm (inset), respectively.

In the presence of molecular oxygen, solvated electrons and H^{\cdot} atoms are known to be efficiently scavenged by molecular oxygen, yielding $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$, eqns. (4) and (11), respectively. Moreover, in strongly alkaline solutions, OH^{\cdot} radicals formed in the primary photochemical steps efficiently react with OH^- ions yielding $\text{O}^{\cdot-}$, eqn. (13), which in the presence of molecular oxygen yields $\text{O}_3^{\cdot-}$ radical ions in a reversible reaction [eqns. (20) and (24)]. In fact, the absorption spectrum observed for irradiation wavelengths > 300 nm agrees with that reported for $\text{O}_3^{\cdot-}$ ^{10–15} and the build-up signal observed at 270 nm can be assigned to the absorption of $\text{O}_2^{\cdot-}$, which is known to be relatively highly stable in alkaline solutions (free of catalytic amounts of metal impurities which may catalyse its decomposition).¹⁶

The participation of reactive HO^{\cdot} , H^{\cdot} and e^-_{aq} during flash photolysis of KOH solutions resembles the radiation chemistry of aqueous solutions and so the extensive information reported on these systems can be used. A set of well established reactions reported in the literature and involving the species present in the irradiated system are listed in Table 1.^{17–19} Those reactions whose participation was considered to

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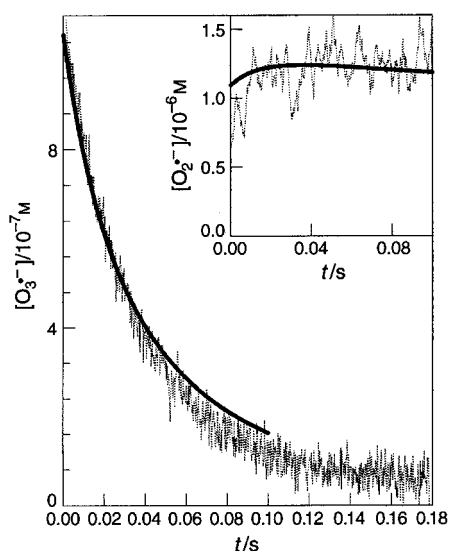


Fig. 2 Experimental (---) and simulated (—) absorbance traces for absorption curves as obtained for $O_3^{\cdot-}$ decay (440 nm) and $O_2^{\cdot-}$ build-up at 270 nm (inset) in 1 M KOH containing 2.5×10^{-4} M O_2 . Optical path length 20 cm, $\epsilon(O_3^{\cdot-})_{440\text{ nm}} = 1900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $\epsilon(O_2^{\cdot-})_{270\text{ nm}} = 1360 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ were used in the calculations

Table 1 Important reactions taking place during UV irradiation of alkaline water

Reaction	Rate constant $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$H_2O + h\nu \rightarrow HO^{\cdot} + H^{\cdot}$ (1a)	
$H_2O + h\nu \rightarrow HO^{\cdot} + H^{\cdot} + e^-_{aq}$ (1b)	
$HO^{\cdot} + h\nu \rightarrow HO^{\cdot} + e^-_{aq}$ (2)	
$e^-_{aq} + e^-_{aq} (+ H_2O) \rightarrow H_2 + 2HO^{\cdot-}$ (3)	5.5×10^9
$e^-_{aq} + O_2 \rightarrow O_2^{\cdot-}$ (4)	1.9×10^{10}
$e^-_{aq} + H^{\cdot} \rightarrow H_2 + HO^{\cdot-}$ (5)	2.5×10^{10}
$e^-_{aq} + HO^{\cdot} \rightarrow HO^{\cdot-}$ (6)	3.0×10^{10}
$e^-_{aq} + O^{\cdot-} (+ H_2O) \rightarrow 2HO^{\cdot-}$ (7)	2.2×10^{10}
$H^{\cdot} + H^{\cdot} \rightarrow H_2$ (8)	7.7×10^9
$H^{\cdot} + HO^{\cdot} \rightarrow H_2O$ (9)	7.0×10^9
$H^{\cdot} + OH^{\cdot} \rightarrow H_2O + e^-_{aq}$ (10)	2.2×10^7
$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$ (11)	2.1×10^{10}
$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2 \rightarrow H^+ + HO_2^{\cdot-}$ (12)	5.5×10^9
$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O + O^{\cdot-}$ (13)	1.3×10^{10}
$HO^{\cdot} + O^{\cdot-} \rightarrow HO_2^{\cdot-}$ (14)	$\leq 2 \times 10^{10}$
$HO^{\cdot} + O_2 \rightarrow H_2O + H^{\cdot}$ (15)	4.2×10^7
$HO^{\cdot} + HO_2^{\cdot-} \rightarrow HO^{\cdot-} + HO_2^{\cdot}$ (16)	7.5×10^9
$HO^{\cdot} + O_2^{\cdot-} \rightarrow O_2 + HO^{\cdot-}$ (17)	8.0×10^9
$O^{\cdot-} + H_2O \rightarrow HO^{\cdot-} + HO^{\cdot}$ (18)	1.8×10^6
$O^{\cdot-} + O^{\cdot-} (+ H_2O) \rightarrow HO_2^{\cdot-} + HO^{\cdot-}$ (19)	8.0×10^9
$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-}$ (20)	3.6×10^9
$O^{\cdot-} + H_2 \rightarrow HO^{\cdot-} + H^{\cdot}$ (21)	8.0×10^7
$O^{\cdot-} + HO_2^{\cdot-} \rightarrow HO^{\cdot-} + O_2^{\cdot-}$ (22)	4.0×10^8
$O^{\cdot-} + O_2^{\cdot-} + H_2O \rightarrow O_2 + 2HO^{\cdot-}$ (23)	6.0×10^8
$O_3^{\cdot-} \rightarrow O^{\cdot-} + O_2$ (24)	$3.6\text{--}6.0 \times 10^{39}$
$O^{\cdot-} + O_3^{\cdot-} \rightarrow O_2^{\cdot-} + O_2^{\cdot-}$ (25)	8.0×10^8
$HO^{\cdot} + O_3^{\cdot-} \rightarrow H^+ + 2O_2^{\cdot-}$ (26)	1.1×10^{10}
$O_2^{\cdot-} + O_2^{\cdot-} \rightarrow O_2 + HO^{\cdot-} + HO_2^{\cdot-}$ (27)	$< 10^2$
$O_3^{\cdot-} + O_2^{\cdot-} + H_2O \rightarrow 2HO^{\cdot-} + 2O_2$ (28)	5.0×10^4

^aUnits: s^{-1} .

be negligible under our experimental conditions were omitted for simplicity. A detailed discussion on some of these reactions and on the establishment of $HO^{\cdot}/O^{\cdot-}$ and $O_3^{\cdot-}/O^{\cdot-}$ equilibria conditions can be found elsewhere.²⁰ An *ab initio* computer program based on the numerical resolution of the differential equations system by the Runge Kutta method was used in order to simulate the reaction kinetics.²⁰ The program considers the flash emission as a delta function, producing HO^{\cdot} radicals, hydrogen atoms and hydrated electrons. The initial concentrations of these transient species

present after the pulse of light were handled as input parameters. According to eqns. (1a,b) and (2), the stoichiometry condition $[HO^{\cdot}]_0 = [H^{\cdot}]_0 + [e^-_{aq}]_0$ was considered. The simulation concentration profiles of $O_2^{\cdot-}$ and $O_3^{\cdot-}$ are not sensitive to the $[e^-_{aq}]_0/[H^{\cdot}]_0$ ratio used as input parameter, as suggested by the participation of the efficient reaction [eqn. (10)] readily converting H^{\cdot} atoms into hydrated electrons. Those $[HO^{\cdot}]_0$ values which best fitted the experimental concentrations of $O_3^{\cdot-}$ were used for the simulations.

The simulated $O_2^{\cdot-}$ and $O_3^{\cdot-}$ concentration profiles obtained at 270 and 440 nm, respectively, are shown in Fig. 2. An acceptable agreement between simulated and experimental profiles supports the proposed mechanism.

Any low-intensity emission of the flash lamp below 200 nm is efficiently absorbed by the water contained in the 0.8 cm pathlength thermostat jacket. Consequently, H_2O photodissociation [eqns. 1(a) and 1(b)] is expected to be negligible and photoionization of $HO^{\cdot-}$ ions [eqn. (2)] should be the main photochemical reaction in the present system.

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