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HYDROGEN PRODUCTION IN PHOTOLYSIS OF AQUEOUS MANGANESE(II) BICARBONATE

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ABSTRACT

Photolysis of an aqueous solution of manganese(II) bicarbonate is found to generate hydrogen with precipitation of manganese(III) hydrous oxide. Manganese(III) hydrous oxide in turn is found to photoreduce water with concomitant oxidation to manganese dioxide. Reaction Mechanisms are discussed.

1. INTRODUCTION

Photoinduced charge transfer in transition metal cations and associated chemical reactions continue to attract attention¹. It is well known that several transition metal ions²⁻⁴ (ie, Fe²⁺, Eu²⁺, Cr²⁺) in aqueous medium when photolysed generate molecular hydrogen with an increase in the oxidation state. The primary photochemical step is formation of a solvated electron (which is scavenged by hydrogen ions) or a hydrogen free radical⁵, ie.

$$X^{n} \quad \frac{hv}{h} > X^{n+1} + e^{-1}$$
(1)

 $X''(aq) \quad -\frac{h\nu}{--} X''^{+1} + OH^{-} + H^{0}$ (2)

Generally (1) occurs only at low pHs and higher pHs favour (2)⁵. Hydrogen evolution results from diffusion controlled combination of H⁰. The rate of hydrogen evolution R [H₂] is largely determined by the rate of back reactions (1) or (2) which influences the probability of combination of H⁰ radicals. If the back reaction is suppressed R[H₂] is enhanced. As an interesting example of this effect, we present our observations on hydrogen production in the photolysis of an aqueous solution of manganese(11) bicarbonate. Detectable quantities of H₂ (ie, above the level observed when water is irradiated with a medium pressure mercury lamp) are not seen when the Mn²⁺ ion is photolysed in aqueous medium at low pH (ie, a solution of MnCl₂ or MnSO₄). However, when a solution of manganese (11) bicarbonate (pH ~ 6) is irradiated with a medium pressure mercury lamp, rapid hydrogen evolution is noted with the precipitation of the oxides of manganese. The reaction occurs because, Mn³⁺ formed in the primary photochemical step is 'instantaneously' hydrolysed to manganese (III) oxide.

2. EXPERIMENTAL

Manganese (II) bicarbonate solution was prepared as follows:

Sodium bicarbonate (0.2M) was added dropwise to a solution of $MnCl_2$ (0.5M) to obtain a pinkish white precipitate of manganese (II) carbonate.

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Precipitate was washed with water, transferred to a flask containing distilled water and the suspension was kept purged with pure carbon dioxide for 45 min. The filtrate gave a solution of manganese bicarbonate containing 1.6×10^{-3} M of Mn²⁺ and pH 6. (Mn content was estimated by precipitation of Mn(OH)₂ with NaOH and ignition of the precipitate at 800°C to obtain ⁶⁻⁷ Mn₂O₃). Photolysis experiments were carried out in an immersion well type photochemical rector (Applied Photophysics) of volume 500 ml. Water cooled (26°C) double-walled inner jacket of the reactor housing the light source (400 W medium pressure mercury lamp) is made from quartz. 350 ml of manganese (II) bicarbonate solution kept in the reactor was rapidly purged with carbon dioxide to remove dissolved oxygen, purging rate was kept constant at a reduced rate (5 ml min⁻¹) and the lamp was switched on. Hydrogen in the out-going gas was detected by gas chromatography (molecular sieve 5A column, thermal conductivity detector). The precipitate formed during photolysis, was dried in vacuum at 90°C and stoichiometry determined by converting it into Mn₂O₃ (all manganese oxides reach the oxidation level Mn₂O₃ on prolonged heating in air at 800°C⁶⁻⁷). X-ray diffractometry (Shimadzu XD-7A X-ray diffractometer) was used to identify the components of the precipitate.

Hydrous manganese oxide was prepared by air oxidation of $Mn(OH)_2^{8-9}$ (made by addition of 0.1M NaOH to 0.1M MnCl₂) at nearly neutral pH. An aqueous suspension of hydrous Mn_2O_3 as prepared by the above method was subjected to photolysis while keeping purged with argon (5 ml min⁻¹). Hydrogen in the out-going gas was monitored by gas chromatography. Precipitate of the same material pressed into pellets (diameter = 13.0 mm, thickness = 1.80 mm, pressure of compactation = 40 MPa) were used for obtaining the Mott-Schottky plots (Hewlett packard LCR Meter 4192 and Kenwood DL-707 digital multimeter were used to measure the capacitance and potential respectively).



Fig. 1 (a) Absorption spectrum of a 1.6 x 10⁻³M solution of manganese (II) bicarbonate irradiated for 15 min.
 (b) Absorption spectrum of 0.1 M solution of Mn²⁺

3. RESULTS & DISCUSSION

Within minutes of irradiation, the nearly colourless solution of manganese (II) bicarbonate acquired a yellowish brown tint (absorption spectrum of the irradiated solution is shown in Fig. 1). On further irradiation colour deepens, however the solution remained transparent for 45 min. At this stage if the lamp is switched off and the solution kept standing for 12 h. a brown precipitate settles down. X-ray diffractometry revealed presence of Mn_2O_3 and small quantities of MnO(OH) and MnO_2 . Oxygen stoichiometry (determined by conversion of the product to MnO_2) was found to be between Mn_2O_3 and MnO_2 , confirming X-ray diffractometry data. When the irradiation is continued for ~ 150 min, the colloidal particles agglomerate into black granules, which settle down immediately if the purging is stopped. After ~ 300 min of photolysis, Mn^{2+} becomes undetectable in the solution. Xray diffractometry showed that the black precipitate is almost entirely MnO_2 . Fig. 2 shows the time variation of the rate of hydrogen evolution during photolysius. It is seen that $R[H_2]$ initially increases with time and then begin to decrease. The above observations can be understood as follows. The primary step in photolysis is the generation of hydrogen free radicals via the reaction,

$$Mn^{2+} + H_2O \rightarrow Mn^{3+} + OH^- + H^0$$
 (3)





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 Mn^{3+} produced in (3) undergoes 'instantaneous' hydrolysis to manganese (III) oxide, hydrous oxide Mn_2O_3 . H_2O and a small quantity of MnO(OH) via,

$$2Mn^{3+} + 3H_2O \xrightarrow{\not{h}} Mn_2O_3 + 6H^+$$
(4)

Combination of hydrogen free radicals generates molecular hydrogen, the net reaction being,

$$2Mn^{2+} + 3H_2O \xrightarrow{h_2} Mn_2O_3 + H_2 + 4H^+$$
 (5)



Fig. 3 The plot of $R[H_2]$ vs time for an aqueous suspension of hydrous manganese (III) oxide ([Mn] 0.02M) Numbers indicated near each curve are the pH values.

The actual ionic species participating in the reaction (5) is the aqua ion¹⁰ $[Mn(H_2O)_6]^{2+}$ having a charge transfer excitation in the vicinity of 325 nm (absorption spectrum shown in Fig. 1). We have observed that (5) does not take place to an appreciable extent when a borosilicate filter that cuts off light ~ 300 nm is used . Occurrence of the reaction is confirmed by the observation, that in the initial stages of photolysis, the precipitate is mainly hydrous manganese (III) oxide. The gradual increase of R[H₂] and further oxidation of the precipitate to MnO₂ results from,

$$Mn_2O_3 + H_2O \xrightarrow{hv} 2MnO_2 + H_2$$
(6)



Fig. 4 Mott-Schottky plot $1/C^2$ vs V (C = capacitance at 500 Hz. v = potential vs SCE). Numbers indicated near each curve are the pH values.

The reaction (6) was confirmed by the observation that photolysis of an aqueous suspension of manganese (III) hydrous oxide yields hydrogen (Fig.3). Possibly the semiconductor property the material (resistivity of the hydrous form dried at 90°C is 2.9 cm and varies with temperature according to the law $r = \rho_0 \exp (E/kT)$ with an activation energy $E \sim 1.9 \text{ eV}$) is responsible for the reaction (6). Photons absorbed generate electron - hole pairs, that participate in the reactions,

2e (conduction ban) +
$$2H_2O$$
 ----> H_2 + $2OH$ (7)

$$2h^+$$
 (valence band) + Mn_2O_3 + H_2O ----- > $2MnO_2$ + $2H^+$ (8)

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Fig. 5 Diffuse reflectance spectrum of manganese (111) Oxide.

Holes are consumed in self-sacrificiation of Mn_2O_3 . The Mott-Schottky plots obtained from compacted pellets of manganese (III) oxide is shown in Fig. 4. The values of flat-band potentials derived from these plots are presented in table 1. Clearly the flat-band potentials are sufficiently negative (ie, less than - 0.6 V vs SCE) for making (7) feasible. Furthermore R[H₂] is found to increase with the increase of pH, because increase of pH makes flat-band potential more negative (Table. 1). The diffuse reflectance spectrum of manganese (III) oxide is shown in Fig. 5. Stronger optical transitions are seen in the region above ~ 350 nm. As expected hydrogen evolution via (6) largely suppressed when a borosilicate filter is used. The mechanism described above could be responsible for precipitation of manganese dioxide from primeval oceans.

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рН	Flat band potential/SCE (V
 07	-0.80
08	-0.85
10	-1.42
12	-1.67
13	-1.75

Table 1 : The flat-band potential of hydrous manganese (III) oxide at different pHs.

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