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Photocatalytic Oxidation of Iodide Ions by Titanium Dioxide

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The photocatalytic oxidation of aqueous I⁻, usually as neutral 0.1 mol kg⁻¹ KI, has been investigated using suspensions of pure anatase and rutile, five doped rutiles and two commercial anatase pigments. Reaction only proceeded in the presence of both O₂ and u.v. radiation to yield I₂, which reacted with excess I⁻ to form I₃⁻; there was no evidence for IO⁻ or IO₃⁻ formation. The dependence of initial reaction rate on the square root of the intensity of the incident 366 nm radiation, together with low quantum yields, reflect the recombinative loss of photoelectrons and photoholes greatly exceeding their consumption in productive reaction steps. No activation energy for I₂ formation was observed with any of the catalysts, and in this respect the photo-oxidation of I⁻ differs from that of liquid alcohols on the identical catalysts. A mechanism is proposed in which I₂ and OH⁻ result from electron transfer between charged and neutral species adsorbed on the TiO₂ surface, leading to an overall reaction:

 $4\mathrm{I}^- + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + h\nu \rightarrow 2\mathrm{I}_2 + 4\mathrm{OH}^-.$

Irradiation of particulate TiO_2 with u.v. light of energy greater than that of the bandgap produces photoelectrons and photoholes within the solid. These photogenerated species may recombine at centres in the bulk or at the surface, but those which are separately trapped at the TiO_2 surface may enter into the reductive and oxidative surface processes which collectively constitute photocatalysis. For sustained photocatalytic reaction electroneutrality must prevail, so that equivalent quantities of both photoelectrons and photoholes must be consumed in the surface processes. It follows that the reactions of interest may be either reductive, oxidative or a combination of both.

In addition to the photosensitized dissociation of water, where the TiO₂ is usually one component of a complex catalyst,¹ numerous other inorganic reactions are photocatalysed by suspensions of anatase or rutile in aqueous solution. These include the reduction of MnO_4^- , $Cr_2O_7^{2-}$ and Fe^{3+} to MnO_2 , Cr^{3+} and Fe^{2+} , respectively,² the oxidation of CN^- to OCN^{-3} and SO_3^{2-} to $SO_4^{2-,3.4}$ and the simultaneous reduction and oxidation of NO to NH_3 , N_2H_4 and $NO_3^{-,5}$ S to H_2S and $SO_4^{2-,6}$ and NH_2OH to NH_3 , N_2 and $N_2O.^7$ Finely divided metals deposited on TiO₂, subsequently used as catalysts or photocatalysts, are generated by the photocatalytic reduction of simple or complex ions.⁸⁻¹⁰ With Pt photodeposited from PtCl_6^{--} the extent of metal dispersion is highly sensitive to the organic reagent selected to consume photoholes in sacrificial oxidation.¹¹

Herrmann and Pichat¹² showed that the photocatalytic oxidation of Br⁻ and I⁻ by an aqueous suspension of anatase required the presence of O_2 to yield dissolved halogen at low pH or hypohalite ions at high pH. Rates of I⁻ oxidation were considerably higher than those of Br⁻, whilst there was no evidence for Cl⁻ oxidation. Subsequently Reichman and Byvik¹³ demonstrated the photoproduction of halogen from acidic solutions of Cl⁻, Br⁻ or I⁻ in the presence of O_2 and pure anatase, but the rates were greatly enhanced when platinized anatase was used. The rate of halogen production was

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in the order $I_2 > Br_2 > Cl_2$ with both pure and platinized anatase. We now report a kinetic study of the photo-oxidation of aqueous I^- by pure anatase, pure and cation-doped rutile and two commercial TiO₂ pigments. To avoid the homogeneous production of I_2 at low pH^{12,13} and the production of IO⁻ at high pH,¹² measurements were normally made using solutions that were initially neutral.

Experimental

Photo-oxidation of I⁻ was investigated using apparatus that has already been described.¹⁴ Unless stated otherwise, 0.2 g of TiO₂ was suspended in 20 cm³ of 0.1 mol kg⁻¹ KI (AnalaR salt in triply distilled water) by a motor-driven stirrer. The partial pressure of O₂ above the reaction mixture was normally maintained at 1 atm (*ca.* 10⁵ Pa), but lower values were obtained by mixing metered flows of O₂ and N₂ and passing 50 cm³ min⁻¹ through the gas space of the reaction vessel. To ensure equilibration of O₂ between gas and reaction mixture phases, the appropriate gas was passed for 30 min before commencing irradiation with filtered 366 nm u.v. light from a Thorn ME/D 250 W medium-pressure mercury lamp. Uranyl oxalate actinometry, taking $\Phi = 0.49$,¹⁵ showed that the unattenuated radiation entering the reaction vessel from the three lamps used was 4.5×10^{-7} (lamp 1), 3.2×10^{-7} (lamp 2) and 2.7×10^{-7} (lamp 3) mol s⁻¹.

In the presence of a considerable excess of I⁻, the I₂ formed in the photo-oxidation was predominantly present as I₃⁻; this ion has an electronic transition at 353 nm ($\varepsilon = 2.6 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$) which forms the basis of the analytical method for I₂. Following extraction and centrifuging, 0.2 cm³ samples of reaction mixture were added to 0.2 cm³ of 0.1 mol kg⁻¹ KI and the absorbance of the resulting solution determined at the observed maximum absorption at 350 nm with a Pye-Unicam SP1800 spectrophotometer using 1 mm cells. The concentration of I₂ formed in the reaction mixture was given by a calibration plot obtained by measuring the 350 nm absorbance of standard I₂ solutions in 0.1 mol kg⁻¹ KI. Observation of the same absorbance when a further 0.2 cm³ sample of the centrifuged reaction mixture was added to 0.2 cm³ of 0.1 mol kg⁻¹ KI in dilute sulphuric acid confirmed that no IO⁻ or IO₃⁻ had been formed.

All TiO₂ samples were from the identical preparations¹⁶ used to investigate photooxidation of propan-2-ol;¹⁴ their specific surface areas are given in table 1. Sufficient pure anatase and pure rutile for all experiments was given three washings with triply distilled water, centrifuged and dried at 375 K before use.

Results and Discussion

Reaction Rates and Conditions

Reaction progress plots of iodine concentration against time were curved for all TiO_2 samples studied. This progressive fall in reaction rate arose from the absorption of 366 nm radiation by the I₃⁻ formed, so that the effective radiation intensity fell with the progress of reaction. In order that activities could be compared, initial reaction rates were determined by computer-fitting data, from not less than five analyses taken over a reaction time of 75 min, to a curve described by a polynomial of the fourth power in time. Since the curve was forced to pass through the origin, the initial rate, in mol kg⁻¹ s⁻¹, was given by the gradient at that point.

Preliminary experiments with pure anatase using lamp 1 showed that the simultaneous presence of TiO₂, 366 nm radiation and O₂ was necessary for the photo-oxidation of I⁻. Initial rates of iodine formation at 293 K were unaffected by (a) ultrasonic treatment of the reaction mixture prior to irradiation, (b) re-use of the anatase following water washing and drying at 393 K and (c) coating the reaction vessel, apart from a window to admit radiation, with either a bright silver mirror or u.v.-absorbing paint. We conclude that the anatase was adequately dispersed by the stirrer, that the solid surface

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| catalyst | surface | lamp | initial rate at 293 K/10 ⁻⁸ mol kg ⁻¹ s ⁻¹ |
|---|---------------|------|---|
| | $/m^2 g^{-1}$ | | |
| pure rutile | 3.6 | 2 | 17.8 ^a |
| rutile/0.1 mol % Cr _a O ₃ | 5.5 | 2 | < 0.01 |
| rutile/0.1 mol % Fe ₃ O ₃ | 4.4 | 2 | 8.2 |
| rutile/0.1 mol % NiÕ | 7.1 | 2 | 4.7 ^b |
| rutile/0.1 mol % Nb ₂ O ₅ | 5.5 | 2 | 13.9 |
| rutile/0.1 mol % WO, | 5.1 | 2 | 13.4 |
| pure rutile | 3.6 | 1 | 24.8^{a} |
| pure anatase | 3.7 | 1 | 22.8^{a} |
| uncoated anatase pigment | 10.2 | 1 | 22.3^{b} |
| coated anatase pigment | 12.0 | 1 | 3.1 |

Table 1. Surface areas and initial rates of I, formation

^a Temperature-independent over range 278–313 K. ^b Temperature-independent over range 293-313 K.

was not materially altered during photo-oxidation and that all 366 nm radiation entering the reaction vessel was absorbed by the anatase.

Turnover Numbers and Reaction Stoichiometry

Total turnover number achieved per surface site can be used to assess whether a photoassisted reaction is truly photocatalytic or is limited to reaction of a monolayer.¹⁷ Calculations are based on an active site concentration of 5×10^{18} m⁻², which is a good measure of a monolayer although it may exceed that of photocatalytic centres by as much as a factor of 10^2 . It follows that total turnover numbers represent minimum values for photocatalysis. Reactions of 75 min duration with 0.2 g of TiO₂ were primarily designed to determine initial rates, and total turnover numbers achieved in these were inconclusive. However, reduction of the TiO_{2} content to 0.015 g or extension of the reaction time to 12 h gave total turnover numbers for I^- ions that were > 10 for both pure anatase and pure rutile. Such turnover numbers confirm the photocatalytic nature of the reaction.

The photoproduction of I_2 was accompanied by the generation of OH⁻, which was quantified from observed changes in pH. Fig. 1 shows that $[I_{o}]/[OH^{-}]$ at the end of an experiment increased with catalyst mass. This is attributed to the preferential absorption of OH⁻ on the oxide surface, which is stronger with anatase than with rutile and is enhanced by providing a greater surface area for absorption. Extrapolation of the plots in fig. 1 to zero catalyst mass gives a limiting value for $[I_{\circ}]/[OH^{-}]$ of 0.5, which is in accord with an overall reaction stoichiometry of

$$2KI + H_2O + O_2 \rightarrow 2KOH + I_2. \tag{1}$$

Reaction progress plots and initial rates with 0.2 g of either anatase or rutile were independent of the initial pH of the reaction mixture over the range 7.0-10.6, which encompasses all pH changes associated with the results presented in fig. 1. This, together with the failure to detect any IO^- or IO_3^- formation in these experiments, support the general validity of eqn (1) in the present work.

Kinetic Studies with Pure Anatase and Pure Rutile

The effect of varying the mass of catalyst on the initial reaction rate at 293 K was determined for anatase with lamp 2 and for rutile with lamp 3. Fig. 2 shows an increase

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Fig. 1. Concentration ratios $[I_2]/[O\overline{H}]$ at the end of reactions at 293 K with lamp 1 as a function of catalyst mass: \bigcirc , anatase; \bigcirc , rutile.



Fig. 2. The initial rate of I_2 formation at 293 K as a function of catalyst mass: \bigcirc , anatase (lamp 2); \bigcirc , rutile (lamp 3).

in activity with catalyst mass, with some values exceeding those observed with 0.2 g of catalyst, although experiments with coated reaction vessels indicated complete absorption of radiation with this mass. This is attributed to the polydisperse nature of the catalysts, where a higher concentration of small particles can lead to a more efficient utilization of absorbed radiation.^{14,18} Nevertheless, in the absence of a well defined limiting activity, a catalyst mass of 0.2 g provides a suitable basis for comparative measurements in all subsequent experiments.

Fig. 3 shows that variation of the reaction temperature between 278 and 313 K had no effect on the reaction progress plots and initial rates with both anatase and rutile. Temperature-independent reaction rates were also observed at an I⁻ concentration of 6.0 mol dm^{-3} and at an O₂ pressure of 0.21 atm, showing that an apparent activation energy of zero generally held for I⁻ oxidation. This is a notable difference from the

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Fig. 3. Reaction progress curves for I₂ formation at different temperatures. Anatase (lamp 2): \bigcirc , 283; \bigcirc , 293; \triangle , 301; \triangle , 308; \bigtriangledown , 313 K. Rutile (lamp 3): \bigcirc , 278; \bigcirc , 288; \triangle , 293; \triangle , 303; \bigtriangledown , 313 K.

photo-oxidation of propan-2-ol on the same catalysts,¹⁴ where activation energies of 31 ± 1 and 26 ± 1 kJ mol⁻¹ were observed for anatase and rutile, respectively. The ratedetermining process in I⁻ oxidation is thus unlikely to be that of trap-hindered transport of photoelectrons, which is considered to be responsible for the activation energy in the photo-oxidation of alcohols.¹⁴

Initial reaction rates at 293 K were determined as a function of the intensity of radiation entering the reaction vessel for anatase with lamp 2 and for rutile with lamp 3. Variations in intensity were obtained using neutral density filters. Plots of initial reaction rate against (intensity)^{0.5} were straight lines passing through the origin, showing that the loss of photoelectrons and photoholes through recombination outweighed their consumption in the surface processes of photocatalysis.^{14,19} Since all radiation entering the reaction vessel was absorbed by the 0.2 g of catalyst it is possible to express the results in terms of quantum yields for I⁻ oxidation, where Φ is given by twice the initial rate of I₂ formation expressed in mol s⁻¹ divided by the radiation intensity. Logarithmic plots of Φ against intensity are given for the oxidation of both I⁻ and propan-2-ol¹⁴ in fig. 4, where a common slope of -0.52 is in good agreement with rates that varied with (intensity)^{0.5}. The plots show that Φ values at the same radiation intensity are closely similar for anatase and rutile of comparable area and purity, although the value for I⁻ oxidation was consistently 0.18 of that for propan-2-ol oxidation.

The effect of oxygen pressure on the initial reaction rate at 293 K was determined for anatase with lamp 2 and for rutile with lamp 3. Fig. 5 shows that plots of $p_{0_2}/(\text{initial rate})$ against p_{0_2} are linear except for the lowest pressure, whereas plots of $p_{0_2}^{0.5}/(\text{initial rate})$ against $p_{0_2}^{0.5}$ were curved. This indicates that molecularly adsorbed oxygen, which obeys the Langmuir isotherm, is involved in I⁻ oxidation as in propan-2-ol

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Fig. 4. Quantum yields at 293 K as a function of radiation intensity. I⁻ oxidation: ●, anatase; ○, rutile. Propan-2-ol oxidation: ▲, anatase; △, rutile.



Fig. 5. Langmuir plots describing the effect of oxygen pressure on initial rates at 293 K: ●, anatase; ○, rutile.

oxidation.¹⁴ Langmuir absorption coefficients of 4.2 atm^{-1} for anatase and 3.3 atm^{-1} for rutile give coverages of 81 and 77% at the standard condition of $p_{0_2} = 1$ atm. The value of 77% is in good agreement with the 82% coverage found for propan-2-ol oxidation on the same rutile sample,¹⁴ suggesting that the oxygen-absorbing sites are the same in both photocatalytic reactions.

The effect of iodide concentration on the initial reaction rate at 293 K was determined for anatase with lamp 1 and for rutile with lamp 3. The shape of the plots in fig. 6 indicates that reaction involves adsorbed iodide ions and that these are more readily adsorbed on anatase than on rutile. However, the data did not obey any of the standard

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Fig. 6. The initial rate of 293 K as a function of iodide concentration: ●, anatase; ○, rutile.



Fig. 7. The initial rate at 293 K as a function of initial iodine concentration with lamp 1: \bullet , anatase; \bigcirc , rutile.

absorption isotherms, whereas Herrmann and Pichat¹² found the Langmuir isotherm applicable at lower I⁻ concentrations on high-area anatase. Additional experiments with rutile showed the cation to be unimportant, in that identical initial rates were obtained from either KI or NaI solutions of the same concentration.

In contrast to the effects of iodide concentration, the addition of low concentrations of iodine to the reactant solution reduced the rate of reaction. Fig. 7 shows that plots of log (initial rate) against initial iodine concentration are linear, which follows from the I_3^- obeying the Beer-Lambert law in competing with TiO₂ for the absorption of 366 nm radiation. The slope of the plots is $-\varepsilon x/2$, where ε is the molar absorption coefficient of I_3^- , x is the effective path length over which photocatalysis occurs and the factor 2 arises from the variation of initial reaction rate with (radiation intensity)^{0.5}. Using an experimentally determined value for ε of 2.04×10^3 m² mol⁻¹ at 366 nm this leads to values for x of 2.2 mm for anatase and 1.9 mm for rutile. Consequently all incident radiation is absorbed within a short distance inside the reaction vessel, reflecting the high absorbtivity of TiO₂ for 366 nm radiation. The present values of x are in

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reasonable agreement with the value of 0.7 mm calculated for the same concentration of rutile suspended in propan-2-ol in the identical reaction vessel.¹⁴

Activities of Doped Rutiles and Anatase Pigments

Table 1 presents activities at 293 K for pure and doped rutile and for pure and pigmentary anatase. Doping rutile with transition-metal ions of valence other than four gave lower activities which were temperature independent over the range 293–313 K. The absence of an activation energy supports a rate-determining step for I⁻ oxidation other than activated transport of photogenerated species through the TiO₂. Whilst the diminished activities suggest that transition-metal ions act as recombination centres so that less photoelectrons and photoholes are available for productive reactions on the TiO₂ surface. There is little difference in activity between pure anatase, pure rutile and uncoated anatase pigment, but that of the coated anatase pigment is considerably less. The SiO₂/Al₂O₃ coating on the latter pigment does not absorb the u.v. radiation, but acts as an insulating barrier against photoelectron and photohole transfer. Presumably the low activity observed arose either from limited penetration of the barrier or from gaps in an imperfect coating.

Mechanistic Considerations

In aqueous suspension the TiO_2 surface is extensively hydrated with surface hydroxyl groups of both cationic and anionic origin and with molecular water both coordinated to exposed Ti⁴⁺ ions and hydrogen-bonded to surface hydroxyl groups.^{20, 21} Iodide ions are only weakly adsorbed from aqueous solution and are unlikely to be directly bound to the TiO₂.²² Oxygen chemisorption will also be limited owing to the low concentration of thermal electrons in TiO₂.

Since IO⁻ formation was not detected in the present work, the mechanism proposed by Herrmann and Pichat¹² is inapplicable, whilst Reichman and Byvik¹³ do not proceed beyond half-cell reactions on platinized anatase. We propose that the initial reaction steps are the same as in the photocatalytic oxidation of alcohols:¹⁴

$$TiO_2 + hv \to h - e \to h + e \tag{2}$$

$$h + e \rightarrow thermal energy$$
 (3)

$$h + OH^{-}(s) \rightarrow OH(ads)$$
 (4)

$$e + O_2(ads) \to O_2^-(ads)$$
⁽⁵⁾

$$O_2^{-}(ads) + H_2O \rightarrow OH^{-}(s) + HO_2(ads).$$
(6)

The absorption of a photon in step (2) generates a photoelectron and a photohole which may recombine in step (3), or be surface trapped to yield $\dot{O}H(ads)$ in step (4) and $O_2^-(ads)$ in step (5). Subsequent reaction of $O_2^-(ads)$ with water in step (6) yields $H\dot{O}_2(ads)$ and regenerates $OH^-(s)$. E.s.r. spectroscopy of spin-trapping adducts has identified the generation of both $\dot{O}H$ and $H\dot{O}_2$ by the u.v. irradiation of aqueous TiO_2 by the u.v. irradiation of aqueous TiO_2 suspensions.²³ Oxidation of weakly bound I⁻(ads) can occur by electron transfer to $\dot{O}H(ads)$ and $H\dot{O}_2(ads)$:

$$\dot{O}H(ads) + I^{-}(ads) \rightarrow OH^{-}(ads) + I(ads)$$
 (7)

$$HO_2(ads) + I^-(ads) \rightarrow HO_2^-(ads) + I(ads).$$
 (8)

Further electron transfer between $HO_2^-(ads)$ and $I^-(ads)$ is unlikely, but interaction with H_2O (ads) yields H_2O_2 (ads):

$$HO_{2}^{-}(ads) + H_{2}O(ads) \rightarrow H_{2}O_{2}(ads) + OH^{-}(ads).$$
(9)

Subsequent reaction of electrostatically neutral $H_2O_2(ads)$ with I⁻(ads) may proceed by step (10) followed by $\dot{O}H(ads)$ reacting by step (7):

$$H_{2}O_{2}(ads) + I^{-}(ads) \rightarrow OH^{-}(ads) + \dot{O}H(ads) + I(ads).$$
 (10)

Following desorption of $OH^{-}(ads)$ and combinative desorption of I(ads), steps (2)–(10) regenerate $OH^{-}(s)$ and give the overall reaction

$$4I^{-} + O_{2} + 2H_{2}O + h\nu \rightarrow 2I_{2} + 4OH^{-}, \qquad (11)$$

which agrees with the experimental stoichiometry of reaction (1).

The experimental quantum yields for I_2 fall considerably short of the upper limiting value of 2 given by reaction (11), which emphasizes the predominant loss of photoelectrons and photoholes by recombination. With the photocatalytic oxidation of alcohols on the same TiO₂ samples, the activation energy was associated with the traphindered migration of photoelectrons to the oxide surface.^{14, 24} The absence of an activation energy for the present reaction suggests that both photoelectrons and photoholes arrive at the oxide surface faster than they can be consumed in non-activated electron-transfer steps which lead to I_2 formation. The excess of photoelectrons and photoholes may then be lost either by step (3) taking place at recombination centres at the surface or by the interaction of trapped species according to:

$$\dot{O}H(ads) + O_2(ads) \rightarrow OH^-(s) + O_2(g).$$
 (12)

The surface enrichment of transition metal ions in doped rutile¹⁶ provides additional surface recombination centres and thus a lower activity without effect on the temperature-independent nature of the reaction. This is in contradistinction to the photo-oxidation of propan-2-ol, where the same doped rutiles yielded activation energies above that of pure rutile.¹⁴

The disparities observed between the photocatalytic oxidation of I⁻ and of alcohols are explicable in terms of different extents of absorption on a hydroxylated TiO₂ surface. Weak adsorption of I⁻ from aqueous solution permits extensive loss of photoelectrons and photoholes by surface recombination, which leads to low quantum yields and the absence of an activation energy. With undiluted alcohols near monolayers of either alkoxide ions or hydrogen-bonded molecules inhibit surface recombination, leading to relatively high quantum yields and an activation energy which reflects photoelectron trap depths within the TiO₂.

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