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# Photoadsorption and Photocatalysis at Rutile Surfaces

## I. Photoadsorption of Oxygen

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A study has been made of the manner in which oxygen is adsorbed on the surface of titanium dioxide (rutile) under the influence of illumination in the near uv ($\lambda > 300$ nm). It has been shown that the presence of adsorbed water enhances the photoadsorption process, and that rutile which has been subjected to prolonged outgassing at high temperature followed by reoxidation in dry oxygen is inactive. The activity can be partially restored by exposing the dry specimen to water vapor. The kinetics of oxygen photoadsorption conform to a parabolic law and it is suggested that a surface-controlled diffusion process is the slow step. A mechanism involving $OH^-$ ions as traps for photo-holes produced by the illumination has been proposed as being the manner in which "adsorbed water" participates in the process, the photoelectrons remaining free to interact with weakly held molecular oxygen.

An important observation is the occurrence of a "memory effect" by which the specimen recovers in the dark the activity it progressively loses during the primary illumination. If the specimen is left in the dark for sufficient time (>16 hr) the activity can be enhanced to a value greater than that of the original specimen. This effect is interpreted as being due to the formation, in the dark, of hole traps of a greater efficiency than the original $OH^-$ ions, and $HO_2^-$ ions are considered to be the species responsible.

## INTRODUCTION

The photocatalytic properties of titanium dioxide were first reported about 50 yr ago by Renz (*1*) who observed that such materials as glycerol, tartaric acid and mannose were photooxidized in its presence while itself becoming darkened and presumably reduced. A reversible phototropic effect was observed by Parmalee and Badger (*2*) who reported that certain ceramic glazes containing rutile darkened when exposed to strong sunlight but recovered their normal color when placed again in the dark. More recently a study of the photooxidation of silver ions adsorbed upon titanium dioxide has been reported by Clark and Vondjidis (*3*), while Boehm and Kaluza (*4*) have discussed the photooxidation of mercury under similar conditions. The important fundamental aspect of the majority of the reported observations is that the processes can only be sustained for long periods of time in the presence of gaseous oxygen. Reactions appear to occur to a limited extent in the absence of oxygen gas but at the expense of reducing the surface of the titanium dioxide.

There have been a few studies of the photoadsorption of oxygen on titanium dioxide surfaces (*5–7*) in which the adsorption kinetics have been related to associated changes in electrical conductivity. ESR studies of samples undergoing photosorption of oxygen have recently been reported by Fukuzawa, Sancier and Kwan (*8*) and Gravelle *et al.* (*9*) invoking the formation of the $O_2^-$ radical ion. Photoadsorption and

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photocatalysis have also been discussed in reviews by Stone (*10*) and by Kwan (*11*).

A decisive mechanism for the photoadsorption of oxygen on titanium dioxide has yet to be devised. However, from the manifold reports of photoeffects it has become apparent that the presence of water enhances the process. It has been observed that phototropic effects with titanium dioxide were much more evident in the presence of water vapor (*12*), the breakdown of films of linseed oil took place more readily in the presence of water (*13*) and a similar effect was observed with the oxidation of mercury (*4*). Solonitsyn and Terenin (*14*) observed that the photosorption of oxygen upon well degassed silica gel took place more slowly than after pretreating the specimen with water vapor.

Only one paper (*15*) appears to have been published on photoeffects which deals exclusively with the interaction of water vapor and oxygen on titanium dioxide; hydrogen peroxide is reported as being produced. The existence of peroxy groups was demonstrated by the ability of the solid to hydroxylate benzene. It is well established, however, that hydrogen peroxide is formed when an aqueous suspension of ZnO is illuminated with ultraviolet light and under similar conditions it would appear likely that $TiO_2$ could behave similarly.

The present work seeks to confirm the role of water in the photoadsorption of oxygen, to measure the extent of the photo-uptake, and to attempt to identify the species produced under uv illumination.

## EXPERIMENTAL METHODS

### *1. Materials*

Titanium dioxide powders were supplied by British Titan Products Co. Ltd. and designated as follows:

a. Rutile (4.1 $m^2\ g^{-1}$), prepared by hydrolysis of titanyl sulfate followed by calcining in air at 1073 K for 5 hr.

b. Anatase (28.4 $m^2\ g^{-1}$), also prepared from titanyl sulfate and calcined at 723 K.

c. Rutile containing 0.3 mol % $Nb_2O_5$ (4 $m^2\ g^{-1}$).

A further sample of rutile was prepared in the laboratory by oxidizing spectroscopically pure titanium sponge (Koch-Light Ltd.) in a small pressure of oxygen at 1073 K.

Oxygen used in both the preparation of the specimens and in the subsequent photoadsorption experiments was prepared by decomposing well outgassed potassium permanganate (A. R. Grade). The oxygen evolved was then adsorbed on a molecular sieve (Linde 5A) at 78 K and finally slowly desorbed from the sieve through three cold traps at 78 K into a 3-liter storage bulb.

### *2. Apparatus*

The adsorption experiments were carried out in a constant volume system of 120 $cm^3$ capacity (Fig. 1), enclosed in an air thermostat at 300 ± 0.1 K. Pressure changes in the system were measured by a Pirani gauge operating at a constant current of 20 mA. The gauge was most sensitive in the region

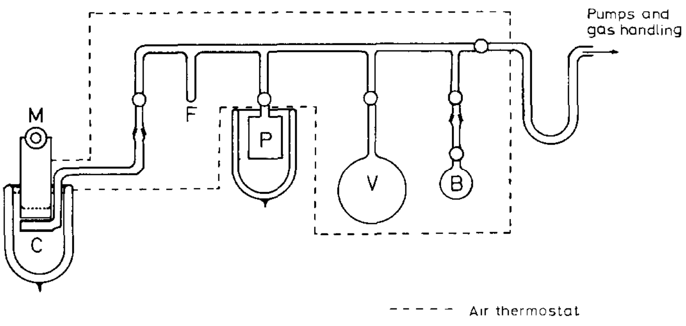

FIG. 1. Photoadsorption system.

0.6 to 4 N $m^{-2}$ and could detect a change of ca. $10^{-3}$ N $m^{-2}$. The adsorption cell C was constructed of silica. It consisted of two optical flats 3 cm in diameter sealed into a silica tube of similar diameter and separated by approximately 1 cm and was attached to the system by a waxed B10 cone and socket.

The specimen, usually 0.5 g, was spread loosely in the cell and was illuminated from above through a Pyrex glass window by a medium pressure mercury arc M (Hanovia 500 W). The arc was cooled by an air turbine and exposed to the specimen by opening an aluminum shutter. A layer of water of 2 cm thickness was contained above the Pyrex window to limit the passage of infrared radiation.

The adsorption system was connected to a pumping unit consisting of two mercury diffusion pumps in series backed by a rotary oil pump. Ultimate vacua of the order of $10^{-4}$ N $m^{-2}$ were attainable. All manipulations were made with stopcocks lubricated with Apiezon T grease and the adsorption system was protected from mercury vapor by U-bend cold traps at 78 K.

### *3. Specimen Pretreatment and Photoadsorption Procedure*

The specimen, in an untreated condition, was placed in the adsorption cell and attached to the vacuum system. Except for measurements on this "raw" rutile (in which case the specimen was merely evacuated to ca. $10^{-3}$ N $m^{-2}$ at room temperature), a small furnace at 1073 K was then placed around the cell and the specimen was outgassed for periods varying from 5 min to 200 hr. After outgassing, dry oxygen was admitted at atmospheric pressure and heating was continued for a further period of from 2 to 24 hr. The specimen was then slowly cooled over a 3–4 hr period to the temperature at which the photoadsorption was to be studied and evacuated to ca. $10^{-3}$ N $m^{-2}$.

The procedure for observing photoadsorption was to admit a dose of oxygen to the evacuated specimen to give an initial pressure of ca. 3 N $m^{-2}$, and measurements of pressure were made in the absence of illumination for approximately 30 min. The specimen was then exposed to the uv illumination and the change of pressure as a function of time was recorded. The temperature of the specimen during photoadsorption experiments was maintained constant either with an ice/water mixture or for temperatures above 273 K with a Dewar vessel through which water was circulated from a reservoir, the temperature of which was controlled by a Tempunit to ±0.1 K.

The structures of the specimens were characterized by X-ray powder photography and the surface areas were measured by krypton adsorption at 78 K.

## RESULTS

### *Photoadsorption of Oxygen on Outgassed Rutile*

Figure 2 shows the quantity of oxygen photoadsorbed on rutile ($q$) plotted as a function of the square root of the illumination time ($t$). Curve (a) refers to "raw" rutile merely evacuated at room temperature and curve (b) shows the effect of 5 min outgassing at 1073 K followed by heating in oxygen at atmospheric pressure for 2 hr. There is clearly a marked decrease in the activity of the specimen as a result of the high temperature treatment. The slope of the linear $q$-$t^{1/2}$ plot can be used to define a "parabolic rate constant" $k$ for the photoadsorption. Table 1 shows the accumulative effect of successive heat treatments under the previously mentioned conditions, demonstrating

TABLE 1

EFFECT OF SUCCESSIVE HEAT TREATMENTS ON OXYGEN PHOTOADSORPTION AT 273 K

| No. of heat treatments | Parabolic rate constant ($10^{10}$ $k$/mol $m^{-2}$ $s^{-1/2}$) |
|---|---|
| 0 | 2.48 |
| 1 | 0.32 |
| 2 | 0.26 |
| 3 | 0.22 |
| 4 | 0.18 |

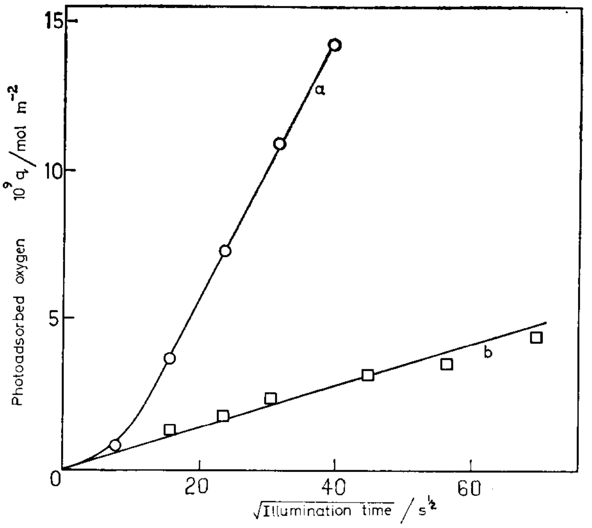

FIG. 2. Oxygen photoadsorption at 273 K. (○) Evacuated at 298 K; (□) outgassed for 300 s at 1073 K and then heated for 2 hr in dry $O_2$.

a progressive but slow decrease in the activity of the specimen.

Table 2 summarizes the effect of increasing the time of evacuation prior to treating the specimen in oxygen and indicates a similar trend to that which is observed in Table 1. The most important observation is that the activity of the specimen for photoadsorption of oxygen can be completely destroyed by prolonged outgassing. A similarly inactive oxide also results by oxidizing titanium sponge in pure dry oxygen.

Physical adsorption of krypton at 78 K on the specimens after these pretreatments indicated that the specific surface area was remaining virtually constant, thus ruling out the possibility of the decrease in the activity being due to marked sintering of the specimen.

TABLE 2

EFFECT OF INCREASING THE OUTGASSING TIME ON OXYGEN PHOTOADSORPTION AT 273 K

| Evacuation time at 1073 K/hr | Parabolic rate constant ($10^{10}\ k$/mol $m^{-2}\ s^{-1/2}$) |
|---|---|
| 0 | 2.48 |
| 0.08 | 0.32 |
| 1.00 | 0.03 |
| 200 | <0.02 |

During experiments in which illumination was maintained for several hours two situations were observed: (i) in the absence of an adequate supply of oxygen the pressure in the system decreased to the value attainable with the mercury diffusion pumps or (ii) in the presence of an excess of oxygen the specimen ultimately became saturated and photosorption ceased, the saturation coverage being $1.75 \times 10^{-7}$ mol $m^{-2}$.

When illumination of the unheated raw material was stopped, the rate of uptake of oxygen was immediately reduced to a small value ($2.6 \times 10^{-12}$ mol $m^{-2}\ s^{-1/2}$). A most significant occurrence was observed if a specimen was illuminated for a second period following an extensive first illumination. Figure 3 illustrates the effect of increasing the "dark interval" between two successive illuminations on the same specimen. Prolonging the interval brought about a marked increase in the rate of oxygen photoadsorption, suggesting that possibly a new process is involved which relies upon changes in the specimen which occur during the dark interval.

### *Desorption Studies*

The immense variation in the activity of the rutile specimens in the photoadsorption of oxygen suggested that it was neces-

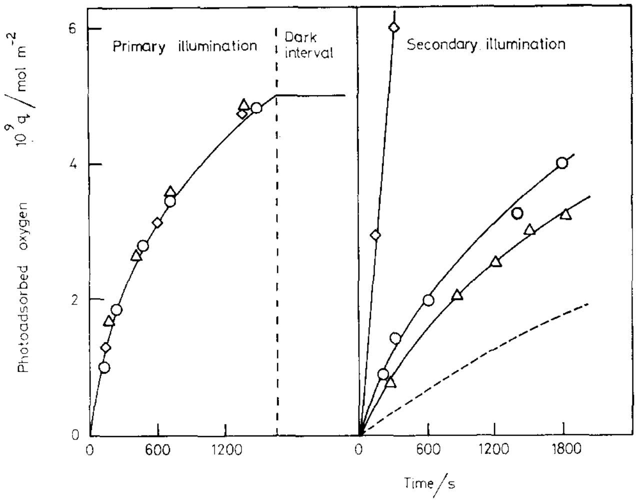

FIG. 3. Effect of dark interval on subsequent oxygen photoadsorption at 273 K. Duration of dark interval: (- - -) 0.08 hr; (△) 0.5 hr; (○) 1.5 hr; (◇) 16.5 hr.

sary to examine the gases being desorbed during the evacuation treatment. For this purpose an additional volume $V$ of 580 cm$^3$ was added to the system (Fig. 1). In the first experiment the raw rutile was outgassed at room temperature. A furnace was placed around the specimen and the temperature was slowly raised to 1073 K. The pressure of gas developed in the closed adsorption system was monitored with the Pirani gauge. When the pressure had reached a steady value the reaction cell was isolated and the cold finger F was successively cooled by a mixture of solid $CO_2$/acetone (193 K) followed by liquid nitrogen (78 K). The resulting partial pressures of gas were ascribed as being due mainly to water vapor, carbon dioxide and to carbon monoxide and oxygen, as confirmed from a further experiment in which the desorbed gases were collected in the sampling bulb B and analyzed by mass spectrometry. A similar experiment was conducted on the specimen which had been subjected to a prolonged evacuation at 1073 K followed by heating and cooling in oxygen.

Table 3 summarizes the results of the two desorption experiments and clearly indicates the large difference in water content of the specimen as a result of the heat treatment.

### *Photoadsorption of Oxygen on Rehydrated Specimens*

A direct test of the importance of water in the photoadsorption process was provided by rehydrating specimens which had been deactived by prolonged outgassing or which had been prepared by oxidizing titanium metal in dry oxygen.

Figure 4 shows a sequence of experiments for the outgassed rutile powder Curve (I) shows the characteristics of the "dry" specimen, curve (II) the behavior of the specimen which had been heated at 1073 K in a

TABLE 3
DESORPTION EXPERIMENTS

| Pretreatment | Gas desorbed/molecules m$^{-2}$ | | |
|---|---|---|---|
| | $H_2O$ | $CO_2$ | $O_2 + CO$ |
| Evacuated at 298 K | $3.0 \times 10^{18}$ | $0.33 \times 10^{18}$ | $0.60 \times 10^{18}$ |
| Outgassed for 17 hr at 1073 K | $0.15 \times 10^{18}$ | $0.16 \times 10^{18}$ | $0.01 \times 10^{18}$ |

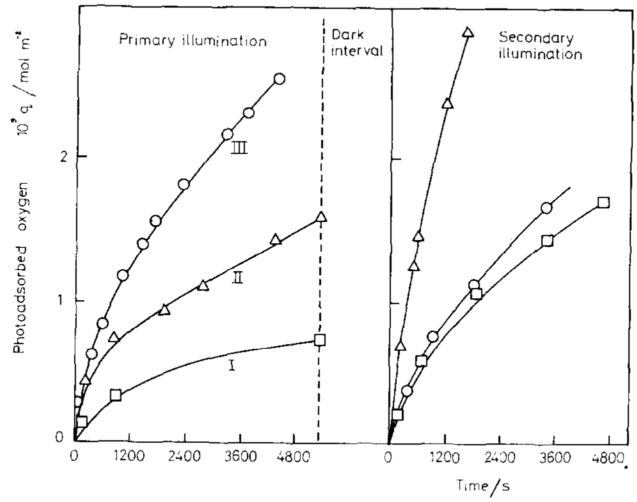

FIG. 4. Effect of water vapor treatment of deactivated rutile on the photoadsorption of oxygen at 273 K. (□) Deactivated rutile (36 hr dark interval) (△) deactivated rutile, heated in 7 N $m^{-2}$ of $H_2O$ vapor and $10^5$ N $m^{-2}$ of $O_2$ for 1 hr at 1073 K (60 hr dark interval) (○) deactivated rutile, heated in 40 N $m^{-2}$ of $H_2O$ vapor and $10^5$ N $m^{-2}$ of $O_2$ for 2 hr at 1073 K (20 hr dark interval).

mixture of ca. 7 N $m^{-2}$ of water vapor and excess oxygen, and curve (III) depicts the behavior following a similar heat treatment with a mixture of ca. 40 N $m^{-2}$ of water vapor and excess oxygen. Similar results were obtained with the oxidized titanium metal.

Three features are evident from the experiments:

a. rehydration brings about an enhancement of the photoactivity of the specimen in oxygen adsorption,

b. the increase in activity of the deactivated specimen following rehydration is not as marked as the decrease in activity of the raw material after outgassing,

c. the "dark recovery" is again present, its extent governing the activity of the specimen during the second illumination.

### *Photoadsorption of Oxygen on Anatase, and Rutile Doped with 0.3 mol % $Nb_2O_5$*

By comparison, the activity per unit area of raw anatase in oxygen photoadsorption was much less than that of raw rutile, the slopes of the corresponding "parabolic" plots being $5.7 \times 10^{-12}$ and $2.5 \times 10^{-10}$ mol $m^{-2}$ $s^{-1/2}$. There was little difference between the activity of raw rutile and the doped rutile, suggesting that either the niobium exists in the lattice as $Nb^{4+}$ ions or that the electronic changes associated with incorporating pentavalent niobium create levels which do not alter the surface electronic structure of the oxide.

## DISCUSSION

It is clear from Fig. 2 and Tables 1 and 2 that outgassing at high temperatures profoundly alters the activity of rutile for oxygen photosorption at 273 K. Since the specific surface area of the specimens does not change with heating, the changing activity must arise through the desorption of species adsorbed on the surface or the loss of lattice oxygen. The desorption experiments (Table 3) in conjunction with a mass spectrometric analysis of the gases desorbed during outgassing indicate that the principal species leaving the raw surface is water, with small amounts of carbon dioxide, carbon monoxide and oxygen. The appearance of $CO_2$, similar in quantity whether raw or outgassed oxide was examined, is considered to arise mainly from the interaction of hydrocarbon vapor from the tap grease with the hot specimen during the desorption test itself. CO production is similarly explained.

Prior to the photoadsorption experiments the outgassed specimens are baked in oxygen at 1073 K, so any oxygen lost during outgassing is replaced and any $Ti^{3+}$ ions are reoxidized to $Ti^{4+}$. The loss of adsorbed water would appear, therefore, to be the important factor governing the decrease in the photoactivity of the rutile specimens. Considerable support is given to this suggestion by the rehydration of deactivated rutile (cf. Fig. 4), whereby the photoactivity is partially restored. It is also noteworthy that several observations are recorded in the literature in which the presence of water or water vapor enhances the ability of titanium dioxide to participate in photoprocesses. The experiments of Korsunovskii (*15*) and Boehm and Kaluza (*4*) illustrate the importance in photocatalysis, while McTaggart and Bear (*12*) have shown that phototropic effects are considerably affected by the presence of water vapor.

A number of papers have been published recently which deal with the adsorption of water on titanium dioxide (both anatase and rutile) and models for the hydrated surface have been proposed (*17–20*). In spite of minor differences, all authors seem to agree that the resulting surface carries weakly and strongly bound molecular water, and hydroxyl groups created by dissociative chemisorption of water. Infrared spectra indicate (*18*) that molecular water is desorbed at lower temperatures than the hydroxyl groups, vestiges of which remain even at 1073 K. Dissociative reaction of water leading to residual $OH^-$ can be envisaged to occur in various ways:

a. Dissociative chemisorption at a surface $Ti^{4+}O^{2-}$ pair leading to $OH^-$ being retained as surface species ($OH_S^-$) (*20*)

$$H_2O + O_S^{2-} = OH_S^- + OH_S^-.$$

b. Dissociative chemisorption of water accompanied by annihilation of preexisting subsurface anion vacancies, $\square_L(O^{2-})$,

$$H_2O + O_S^{2-} + \square_L(O^{2-}) = OH_S^- + OH_L^-$$

producing surface $OH_S^-$ and bulk $OH_L^-$;

c. High temperature dissociative chemisorption of water involving surface or lattice oxide ions ($O_{S,L}^{2-}$) with simultaneous release of oxygen gas

$$2H_2O + 4O_{S,L}^{2-} + 4Ti^{4+} = 4OH_{S,L}^- + 4Ti^{3+} + O_2(g)$$

again producing surface and/or bulk $OH^-$.

The high temperature outgassing treatment employed in the present work leads to the suggestion that it is residual hydroxyls which are responsible for the enhanced photoactivity, particularly when viewed together with the rehydration experiments. Exposure of the specimens to water vapor at 298 K did not bring about any marked increase in the photoactivity of deactivated specimens, whereas the high temperature treatment resulted in a significant enhancement of the photoactivity (Fig. 4).

It is necessary to consider the manner in which the hydroxyls might participate in the photoadsorption process. Rutile is a wide band gap semiconductor ($E_{\text{gap}} = 3.2$ eV) and appreciable photoconductivity can be stimulated only by illumination of energy greater than $E_{\text{gap}}$, i.e., $\lambda < 390$ nm. Under these conditions intrinsic conduction occurs through positive holes (h) in the valence band and electrons (e) in the conduction band.

$$TiO_2 + h\nu \rightleftharpoons \text{h-e(exciton)} \rightleftharpoons h + e.$$

The presence of adsorbed oxygen in the dark causes a space charge to develop at the surface, which under illumination t $\lambda <$ a 390 nm favors the movement of photo-holes to the surface. Here they become trapped at surface states, which in the present experiments we envisage to be residual $OH^-$ ions, so the trapping amounts to conversion to hydroxyl radicals:

$$OH^- + h \rightarrow OH.$$

Once the hole is trapped the photoelectron is free to participate in the adsorption of oxygen:

$$O_{2\text{ads}} + e \rightarrow O_{2\text{ads}}^-.$$

The trapped hole appears to be quite stable since, when the illumination is terminated, no desorption of oxygen occurs. Desorption might have been expected due to the surface diffusion of $O_{2_{ads}}^-$ and hole–electron recombination

$$OH + O_{2_{ads}}^- \rightarrow OH^- + O_{2_{ads}} \rightarrow OH^- + O_2(g).$$

However, the stability of the hydroxyl radical may not be the reason for the absence of desorption during the dark interval following an illumination period. It is observed that the *duration* of the dark interval has a marked effect on the photoactivity of the specimen (Fig. 3), considerable enhancement resulting from a dark interval of 16 hr. It seems likely that during the primary illumination and subsequent dark interval species are created which can act as more efficient hole traps than the original hydroxyl ions. The capture of an electron by the hydroxyl radical would merely regenerate the original hydroxyl ion, which could not lead to any enhancement of the photoactivity. It is possible, however, that the hydroxyl radical reacts with an adsorbed oxygen molecule ion $O_2^-$ arriving by surface diffusion according to the following scheme:

$$OH + O_{2_{ads}}^- \rightarrow HO_2 + O_{ads}^-$$

During the dark interval the perhydroxyl radical $HO_2$ captures an electron to become a perhydroxyl ion and thus form a potential trap for holes generated in a subsequent illumination:

$$HO_2^- + h \rightarrow HO_2.$$

Once again the electron generated in the photoprocess is able to be trapped by adsorbed oxygen. The enhancement in the photoactivity for oxygen adsorption is considered to be due mainly to the difference in efficiency of the two hole-trapping mechanisms. These results are supported by the work of Addiss and Wakim (*7*) and Vohl (*21*) who indicate that a hole-trapping mechanism is necessary to account for their observations. These authors suggest that adsorbed oxygen ions ($O_2^-$ and $O^-$) are probably trapping centers. It seems unlikely to us that this can be the case, since they do not observe photodesorption of oxygen as would be expected if their proposed mechanism were operating. The enhanced photosorption of oxygen during a secondary illumination is quite similar to the "memory effect" described by Volkenstein and Baru (*22*), which is ascribed to the localization of nonequilibrium charge carriers generated by illumination at structural surface defects.

In line with the work of Kennedy, Ritchie and Mackenzie (*5*), the kinetics of the primary photoadsorption of oxygen at 273 K can be described by a parabolic relationship (cf. Fig. 2), which is consistent with a surface diffusion process such as that involving $O_{2_{ads}}^-$ being the limiting factor. This may also partly account for the enhancement in the rate of photoadsorption during the secondary illumination in which surface diffusion may not be necessary. During the photoadsorption process, positive holes are drawn to the illuminated surface by the space charge layer, with the result that the illuminated surface becomes less negatively charged. The dark side of the crystal, on the other hand, experiences an increasing negative charge as $O_{2_{ads}}^-$ ions accumulate. In order to neutralize the unbalance of charge surface diffusion occurs and this may control the rate at which holes are trapped, since it will control the potential gradient in the space charge layer. The saturation coverage of oxygen on raw rutile corresponds to approximately 3% of a monolayer, which although about 30 times larger than the number of sites actually in the beam may represent the total area of those particles on which some illumination is directly incident.

Since no oxygen desorption is observed after the secondary photoadsorption process, it is concluded that the $HO_2$ radical does not capture an electron from the conduction band but reacts instead with a surface species according to a reaction of the type

$$HO_2 + OH^- \rightarrow H_2O + O^-,$$

or

$$HO_2 + HO_2^- \rightarrow H_2O + O_3^-.$$

Anatase in comparison to rutile is much less active in oxygen photoadsorption, although its water content is larger. It is suggested that the difference in activity between the two phases is attributable to the stronger absorption of rutile in the wavelength region near the visible (*23*) and to its better crystallinity favoring energy transfer.

## ACKNOWLEDGMENT

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