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Photoadsorption and Photocatalysis at Rutile Surfaces

II. Photocatalytic Oxidation of Isopropanol

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The photocatalytic oxidation of isopropanol has been studied in a specially designed rotating reaction vessel affording good contact between the incident uv light and the powdered photocatalyst. It has been shown that when TiO_2 (rutile) is illuminated with light of wavelength $\lambda > 300$ nm in the presence of isopropanol vapor and oxygen at 300 K, the primary organic oxidation product is acetone.

When isopropanol is present as a presorbed layer, the kinetics of the evolution of acetone into the gas phase can be studied as a displacement process. The behavior is discussed in detail with reference to the adsorption isotherms of isopropanol, acetone and water on rutile, and the effect which one component exerts upon the adsorption of the other components. Isopropanol and water are both capable of displacing acetone from the surface.

The formation of acetone cannot be sustained in the absence of oxygen, and it is concluded that oxygen photoadsorption is a precursor to the photooxidation. Reaction schemes are discussed.

INTRODUCTION

The phenomenon of photooxidation was observed and recognized in 1921 by Renz (*1*), who was able to oxidize many organic molecules in the presence of TiO_2 and ultraviolet light. Later, Goodeve and Kitchener (*2*) reported that organic dyestuffs could be bleached and Jacobsen (*3*) oxidized linseed oil in a similar manner on TiO_2. Difficulties arise when studying a reaction involving a large organic molecule in as much as there are often many products which can themselves undergo further degradation. It is then an extremely arduous task to decide the true course of the reaction.

Recent studies of the photoadsorption of oxygen upon TiO_2 have shown (*4*) that water, probably in the form of OH ions, is of prime importance in allowing the process to take place, and results in the formation of a surface peroxide species which is presumably responsible for the oxidation of adsorbed organic molecules in the reactions mentioned above.

Several studies of photocatalytic reactions using TiO_2 have been made in solution but those restricted to heterogeneous gas–solid reactions are very few. Filimonov (*5*) has studied the photooxidation of isopropanol to acetone in the presence of TiO_2. The study was made using an infrared spectroscopic method in which the gas phase was monitored and simultaneously the adsorbate on the TiO_2 surface was subjected to a close scrutiny. Acetone was the product detected in the gas phase while tightly adsorbed carboxylate species remained on the surface and could not be removed even after evacuation at 625 K. More recently, Gravelle *et al.* (*6*) have studied the electronic mechanism of the photooxidation of isobutane on TiO_2, concluding that photo-holes are required

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for the interaction between paraffins and photoadsorbed oxygen on TiO_2.

The present work has been carried out with isopropanol and has been designed as an extension of the work already carried out on the photoadsorption of oxygen (*4*) and the adsorption of isopropanol, acetone and water (*7*) on TiO_2, with the intention of applying the knowledge thereby obtained to the photocatalytic oxidation of isopropanol.

EXPERIMENTAL METHODS

Materials

Titanium dioxide powder was supplied by British Titan Products Co. Ltd. as pure rutile (4.2 $m^2\ g^{-1}$) and had been prepared by hydrolysis of titanyl sulfate followed by calcining for 5 hr at 1073 K. The sample was the same as previously used in studies of photoadsorption of oxygen (*4*) and adsorption of organic vapors and water (*7*).

Conductivity water, BDH isopropanol, and acetone employed in photocatalysis were subjected to several freeze–pump–thaw cycles before use. Oxygen preparation was as previously described (*4*).

Apparatus and Procedure

Photooxidation of isopropanol was carried out in a circulating system (1480 cm^3) incorporating the reactor vessel shown diagrammatically in Fig. 1. The reaction was studied either: (i) with a presorbed layer of isopropanol, but no isopropanol in the gas phase, or (ii) with a presorbed layer and isopropanol also in the gas phase.

The production of acetone and the consumption of isopropanol were monitored by sampling the gas phase during the reaction and analyzing with a Perkin-Elmer F11 gas chromatograph. Oxygen consumption was measured by a silicone oil manometer, after isolation from the system and trapping of the vapors in a cold finger. Analyses for water and carbon dioxide were made when discrepancies were observed between the pressure evaluated from the sum of the partial pressures of oxygen, isopropanol and acetone, and the total measured pressure in the reactor.

A charge of TiO_2, usually 20 g, was placed in the tubular reactor vessel (Fig. 1), the interior of which could be rotated at 30 rpm by a magnetic coupling. Glass vanes along the length of the inside tube ensured that as the tube rotated the powder lying in the bottom of the tube was collected and carried upwards. A rectangular window in the side of the vessel enabled the contents to be illuminated by a mercury arc (Hanovia 500 W) along the whole length of the vessel. The part of the vessel not forming the window was covered with an insulated heater coil. The rotation allowed the TiO_2 powder to fall continuously through the illuminated volume, thereby providing maximum contact between the incident light and the solid. At the same time the gas was circulated by a turbine with four stainless steel paddles rotated at 3000 rpm by a magnet attached to a motor. The total pressure employed was about 1.3 kN m^{-2} with oxygen in at least a tenfold excess.

Photooxidation was followed for about 9 hr and then the system was evacuated at

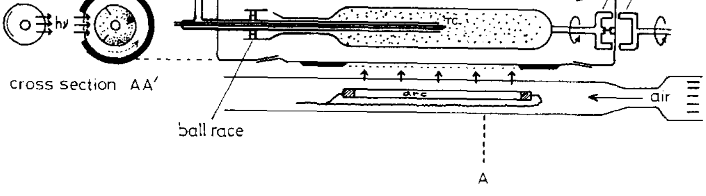

FIG. 1. Photocatalytic reactor vessel, showing the rotating inner parts and the method by which the powdered catalyst is tumbled through the incident light.

room temperature to remove the gas phase and the weakly adsorbed species. The specimen was then heated at 573 K while the desorbed species were condensed in a cold trap in the inlet section of the chromatographic device and subsequently analyzed.

A standard pretreatment temperature of 600 K was selected for the TiO_2 catalyst loaded in the reactor. This was the pretreatment temperature adopted in the adsorption studies previously reported (*7*). The sample was outgassed in the reactor vessel at 600 K for 3–4 hr, heated in oxygen or in dry air (100 kN m^{-2}) at the same temperature and then cooled to the temperature of the experiments (~300 K). According to previous studies (*7*, *8*) the surface of the sample after this treatment may be considered as a combination of Ti^{4+} ions, O^{2-} ions and OH-pairs more or less randomly distributed to give a structural pattern similar to the one expected for the 110 face of rutile about 50% hydroxylated. On this surface, water, isopropanol and acetone are irreversibly adsorbed at room temperature to complete the coordinative unsaturation of the Ti^{4+} ions up to a coverage of $0.33 \pm 0.01 \times 10^{-6}$ m^3 g^{-1}. In addition, adsorption of all three species may occur on the primary layer of OH groups and coordinatively adsorbed molecules, but in a weaker form.

In order to link the results with those on the photoadsorption of oxygen presented in the preceding paper (*4*), the photooxidations in the circulating system were preceded by some experiments in the small, closed volumetric system previously described (*4*). For this purpose, 0.5 g samples of TiO_2 were used. In the first set of experiments, the TiO_2 was outgassed at 1073 K for 2 hr in 100 kN m^{-2} of dry oxygen, and cooled to 273 K. Isopropanol was presorbed to differing coverages on the evacuated surface, and the photo-uptake of oxygen was then investigated using the procedure described earlier (*4*). A trap cooled to 78 K was present in the system to condense any vapor released from the surface during the illumination. These experiments were followed by a similar set in which the TiO_2 was outgassed only at 600 K, the temperature of pretreatment used for the photooxidations in the circulating system.

RESULTS

Photo-uptake of Oxygen on Isopropanol-Covered Surfaces

Adsorption of isopropanol on the specimen pretreated at 1073 K in the volumetric system gave type I isotherms similar to those previously reported for the sample outgassed at 600 K (*7*), though the amount of irreversibly adsorbed alcohol was about 10% lower. In addition, temperature programmed desorption (TPD) experiments showed that desorption of the adsorbed alcohol occurred in this case with partial decomposition to propylene and acetone, contrary to the pure desorption observed from a sample pretreated at 600 K.

Figure 2 shows that photoadsorption of oxygen was enhanced by increasing coverages of isopropanol, while the parabolic law characteristic of the isopropanol-free surface (*4*) passes over to a linear law for a fully isopropanol-covered surface. A rate constant of 2.3×10^{-11} mol m^{-2} s^{-1} can be evaluated from the straight line in Fig. 2. Acetone and

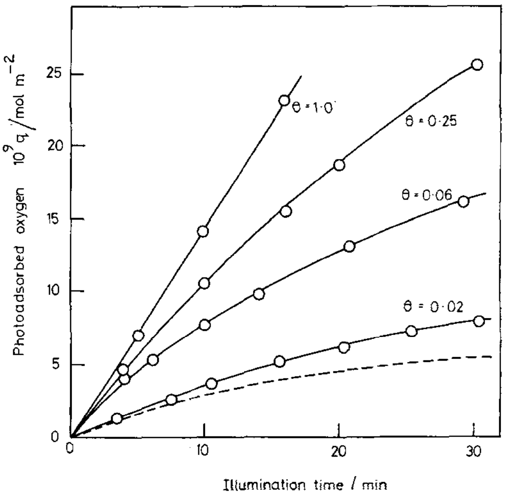

FIG. 2. Photoadsorption of oxygen at 273 K on TiO_2 with different coverages (θ) of adsorbed isopropanol. Monolayer of isopropanol ($\theta = 1$) = 0.33 $\times 10^{-6}$ m^3 g^{-1}. (- -) Photoadsorption of oxygen on an isopropanol-free TiO_2 sample [from (*4*)].

CO_2 were found at the end of these experiments in the cold trap.

A similar set of experiments on TiO_2 outgassed only at 600 K gave comparable results but the rate of photofixation of oxygen was greater, indicating that the greater hydroxyl coverage was responsible for the increase in rate. CO_2 was not found in the cold trap in this case, suggesting that the stronger adsorption of the alcohol on the sample outgassed at 1073 K facilitates the further oxidation of acetone.

Photooxidation of Isopropanol

Plots of the acetone partial pressure developed in the circulating system as a function of time of illumination are shown in Fig. 3 for four different conditions. In (a) and (c) only a monolayer of presorbed isopropanol (0.33×10^{-6} m^3 g^{-1}) was present: in (b) and (d) a pressure of 92 N m^{-2} of isopropanol was also present in the gas phase. In (a) and (b) oxygen was absent: in (c) and (d) oxygen was present at a partial pressure of 1330 N m^{-2}.

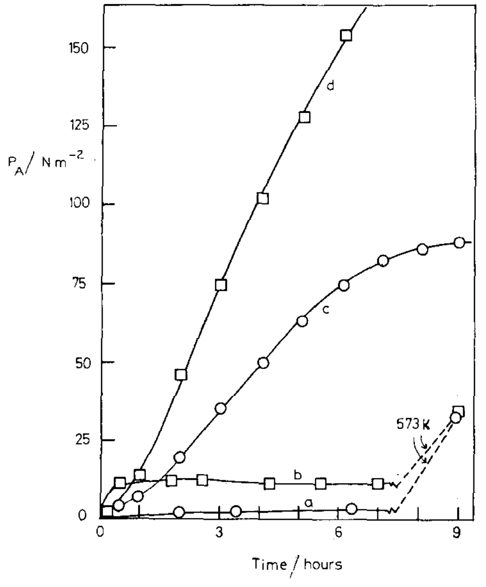

FIG. 3. Evolution of acetone during photooxidation of isopropanol: (a) from a monolayer of adsorbed isopropanol illuminated *in vacuo;* (b) from a monolayer of adsorbed isopropanol and an initial pressure of 92 N m^{-2} isopropanol in the gas phase; (c) and (d) are for the same isopropanol conditions as in (a) and (b), respectively, but also with an initial pressure of 1.33 kN m^{-2} of oxygen in the gas phase.

Experiments (a) and (b) establish that the reaction producing acetone cannot be sustained when there is no oxygen in the gas phase. A small amount of acetone (equivalent to $P_A \sim 35$ N m^{-2}) could be desorbed into the cold trap after 7 hr illumination, but this is very small by comparison with the amount (equivalent to $P_A = 520$ N m^{-2}) which corresponds to the oxidation of the monolayer of isopropanol. In experiments (c) and (d), on the other hand, all isopropanol present in the system was converted into acetone after an appropriate period of illumination.

In spite of the fact that the capacity of the surface for both isopropanol and acetone is known to be the same (7), Expt (c) shows that acetone appeared in the gas phase in appreciable quantity during illumination. Water, which must be generated together with acetone during the photooxidation of isopropanol, does not appear in the gas phase, and its preferential retention is considered to be the reason for the release of acetone. Meanwhile, Expts (b) and (d) show that a vapor pressure of isopropanol enhances the evolution of acetone. These effects are discussed further in the following sections.

Analysis in Expt (c) of the irreversibly adsorbed species after 9 hr of illumination, carried out by heating and collection of the desorbate, showed that water and acetone were the species remaining adsorbed. This indicated that all of the alcohol had been oxidized to acetone.

Displacement of Acetone by Isopropanol Vapor

Figure 4 shows the changes in alcohol, acetone and oxygen pressures in the photoreactor as a function of the time of illumination in three different experiments. Some features are noteworthy in these experiments. Firstly, the evolution of acetone levels off after 7–8 hr of illumination when alcohol was not present in the gas phase

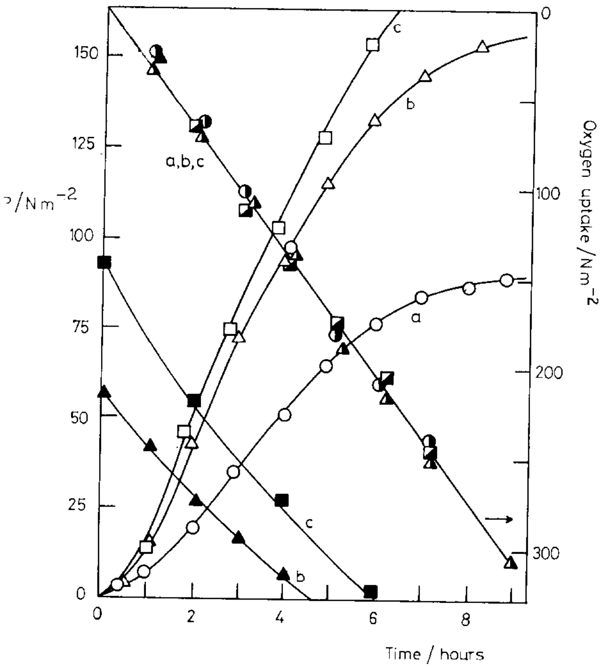

FIG. 4. Evolution of acetone (○, □, △, left scale), pressure fall for isopropanol (■, ▲, left scale) and oxygen uptake (◐, ◪, ◭, right scale) during photooxidation of isopropanol at ~300 K on TiO_2 outgassed at 600 K. (a) From a monolayer of isopropanol but without isopropanol in the gas phase (circles); (b) as (a), but also with an initial pressure of 56 N m^{-2} of isopropanol in the gas phase (triangles); (c) as (a), but also with 92 N m^{-2} isopropanol initially in the gas phase (squares). Initial oxygen pressure in all experiments was 1.33 kN m^{-2}.

[Case (a)]. Secondly, in all three experiments the rate of photo-uptake of oxygen was the same (~34.4 N m^{-2} hr^{-1}) and remained constant throughout all the experiments. This rate (8×10^{-11} mol m^{-2} s^{-1}) was more than three times greater than in experiments in Fig. 2, and is probably due to the different pretreatment of the sample and to better illumination of the reactor vessel. Finally, it was observed that the rate of consumption of isopropanol from the gas phase (12–15 N m^{-2} hr^{-1}) was almost constant with time (zero order in alcohol), though much lower than the rate of oxygen uptake. It was also noticed that the amount of acetone in the gas phase during Expts (b) and (c) was roughly the sum of the amount evolved in (a) plus the amount equivalent to the alcohol consumed from the gas phase at each time, suggesting that the alcohol dislodges acetone from the TiO_2 surface in a 1:1 molar ratio.

Displacement of Acetone by Water

A set of experiments was carried out on a sample which had been outgassed at 600 K and then saturated with 0.31×10^{-6} m^3 g^{-1} of water vapor to complete the coordination of the Ti^{4+} ions at the surface (hereafter termed the "hydrated surface"). An excess of isopropanol was introduced to this sample and then the gas phase was removed by trapping at 78 K. GC-analysis of the trapped vapor confirmed that isopropanol, which was adsorbed up to 0.25×10^{-6} m^3 g^{-1} on this surface, did not displace the coordinatively adsorbed water.

Photooxidation of the adsorbed alcohol was followed in the usual conditions in the presence of ~1.33 kN m^{-2} of oxygen. Figure 5 shows the pressure changes for acetone, alcohol and oxygen in two of these experiments. In (a) only oxygen was present in the gas phase, while in (b) 42 N m^{-2} of

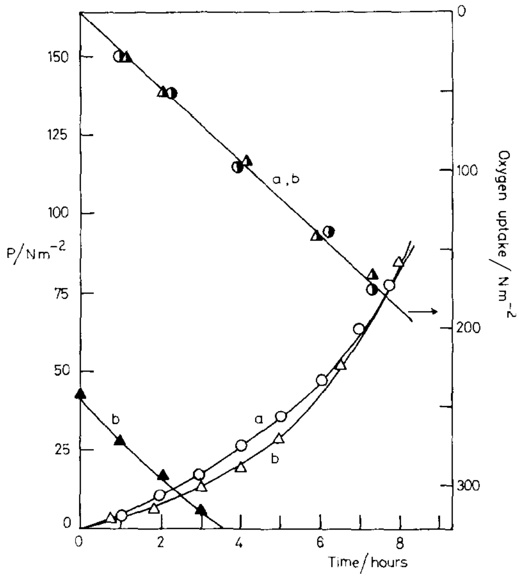

FIG. 5. Changes in partial pressures for isopropanol (▲, left scale) and acetone (○, △, left scale), and oxygen uptake (◐, ◭, right scale) during photooxidation of isopropanol on a "hydrated" surface. Initial oxygen pressure = 1.33 kN m^{-2}. (a) From a monolayer of isopropanol but without isopropanol in the gas phase (circles); (b) as (a), but with 42 N m^{-2} isopropanol and 100 N m^{-2} of water vapor in the gas phase (triangles).

alcohol and 100 N m^{-2} of water were initially in the gas phase together with the oxygen.

Several features are of interest in Fig. 5 in comparison with data in Fig. 4. Firstly, the rate of consumption of oxygen was lower for the hydrated surface although it was also constant throughout the experiments and, as in Fig. 4, it did not depend on the presence of isopropanol in the gas phase. However, the rate of consumption of the alcohol was roughly the same as in Fig. 4, though the evolution of acetone was not enhanced here by the alcohol vapor.

At the end of both experiments in Fig. 5 water was found in the gas phase. In (a) a pressure of 50 N m^{-2} was measured while in (b) the amount of water was 100 N m^{-2} greater than the initial amount introduced. Meanwhile, the analysis of the irreversibly adsorbed phase gave water as the main strongly adsorbed species, which together with the small pressure of acetone evolved during the photoreaction suggests that much of the acetone produced was now being accommodated in a weak form and has been removed during the evacuation at room temperature before analysis of the irreversibly adsorbed species at the end of the experiments.

The effect of water vapor on the evolution of acetone during photooxidation of isopropanol was further studied using a sample outgassed at 600 K and covered with isopropanol. Water vapor was introduced at a pressure of 0.27 kN m^{-2} together with oxygen (~1.33 kN m^{-2}) and the evolution of acetone into the gas phase was followed in the usual way. The evolution plot was the same as in Fig. 4a and reveals that water vapor under these conditions does not displace acetone from the surface, in contrast to isopropanol.

Photooxidation of Acetone

Only traces of CO_2 were detected in the gas phase after 9 hr of illumination of a sample which had been outgassed at 600 K and then covered with a monolayer of irreversibly adsorbed acetone (0.33×10^{-6} m^3 g^{-1}). Nevertheless, oxygen was photoadsorbed at a constant rate of 18.2 N m^{-2} hr^{-1} indicating that acetone was being oxidized. When the experiment was repeated using an excess of acetone in the gas phase, the pressure of acetone did not change during the illumination, suggesting that the oxidation products of acetone remain tightly adsorbed on the surface. The analysis of the irreversibly adsorbed species after 9 hr of illumination showed that acetone was in a great excess on the surface together with water, carbon dioxide and traces of carbon monoxide and formaldehyde.

DISCUSSION

The Electronic Mechanism of Photooxidation

Experiments in Figs. 2 and 3 summarize the most important features of the photooxidation of isopropanol adsorbed on TiO_2 to yield acetone. Figure 2 shows that not only does the rate of oxygen consumption sharply increase when the amount of presorbed isopropanol is increased, but also the parabolic law passes over to a linear law, indicating that isopropanol very rapidly consumes photoadsorbed oxygen and eliminates the surface diffusion step that controls the photo-uptake of oxygen on the original surface of this TiO_2 sample exposed to ultraviolet irradiation (*4*).

The second important conclusion arising from these exploratory experiments is that surface hydroxyl groups appear to act also as intermediates in the photocatalytic oxidation of isopropanol. The sample outgassed at 600 K, which holds more OH groups, has a higher activity than the sample outgassed at 1073 K but which has a comparable isopropanol coverage. This is closely analogous to the previous results of Bickley and Stone (*4*) who found that the photo-uptake of oxygen on this sample depends on the amount of hydroxyls on its surface, which they consider to act as trapping centers for photo-holes according to the reaction,

$$\text{light } (h\nu) + TiO_2 \rightarrow \text{exciton (h–e)}$$

$$\text{exciton (h–e)} + OH_s^- \rightarrow OH_s^{\cdot} + \text{e (free)}$$

In addition to these observations, the data in Fig. 3 prove that oxygen in the gas phase is necessary to sustain the photooxidation, though evidently the small amount of oxygen present as a residue on the surface after the 600 K baking and the evacuation at 300 K can be activated by the light.

On the basis of these statements it is possible to propose a mechanism for the photooxidation of isopropanol in which the initial step, as previously suggested for pure photoadsorption of oxygen on this sample, involves residual OH groups (securely fixed to the surface) as traps for the photo-holes, thus enabling the photoelectrons to form O_2^-:

$$O_2 \text{ (g)} + \text{e (free)} \rightarrow O_2^- \text{ (ads)}.$$

Because there is an abundant coverage of isopropanol on the surface, O_2^- may attack an adjacent isopropanol molecule instead of diffusing to react with the trapped hole, which is the process which occurs in pure photo-uptake of oxygen on this sample. The reaction may be written as a proton transfer:

$$O_2^- + \text{PrOH} \rightarrow HO_2^{\cdot} + \text{PrO}^- \qquad (\text{PrOH} = \text{isopropanol})$$

or as an H-atom transfer:

$$O_2^- + \text{PrOH} \rightarrow HO_2^- + \text{PrO}^{\cdot}$$

so that either of the two following schemes may then occur:

Scheme A:

$$HO_2^{\cdot} + \text{PrOH} \rightarrow H_2O_2 + \text{PrO}^{\cdot}$$

$$H_2O_2 + \text{PrO}^- \rightarrow A + H_2O + OH^{\cdot} + \text{e (to catalyst)}$$

$$OH^{\cdot} + \text{PrO}^{\cdot} \rightarrow A + H_2O$$

(A = acetone)

Scheme B:

$$HO_2^- + \text{PrOH} \rightarrow H_2O_2 + \text{PrO}^-$$

$$H_2O_2 + \text{PrO}^{\cdot} \rightarrow A + H_2O + OH^{\cdot}$$

$$OH^{\cdot} + \text{PrO}^- \rightarrow A + H_2O + \text{e (to catalyst)}$$

Both involve two molecules of isopropanol, one of which reacts as a radical and the other as an anion. In either case the overall reaction is the same, namely:

$$O_2 \text{ (g)} + 2\,\text{PrOH (ads)} + h\nu \rightarrow 2\,A + 2\,H_2O. \qquad (1)$$

So far as the fixed OH_s ions of the surface are concerned, the process is now a chain reaction, the electron going back to the catalyst regenerating the OH_s ion according to

$$OH_s^{\cdot} + e \rightarrow OH_s^-.$$

The ultraviolet output of the arc was of the order of 10^{16} quanta/sec, and only about 20% of the light was incident on the vessel. The quantum efficiency of the reaction can be only roughly estimated from the rate of consumption of oxygen (8×10^{-11} mol m^{-2} s^{-1}) but it appears to be of the order of magnitude of unity. Thus the rate of photocatalytic oxidation of isopropanol seems to be controlled by an efficient photoadsorption of oxygen, followed by a rapid oxidation of the adsorbed alcohol.

Adsorption Equilibria During Photooxidation

The proposed mechanism explains the general observations already outlined but it is not easy to see how it can account for the shapes of the plots for acetone and isopropanol in Figs. 4 and 5. The adsorbed monolayer of isopropanol in Expt (a) in Fig. 4 corresponds to 520 N m^{-2} of acetone. Thus the acetone production is apparently falling off long before the monolayer of isopropanol is converted. Assuming that the water produced according to Eq. (1) remains adsorbed in place of the alcohol which has reacted, there is no need for water to appear in the gas phase, and none was detected. However, the evolution of acetone should not cease until the pressure has reached 520 N m^{-2} unless some of the acetone becomes accommodated on the resulting hydrated surface. The time required for the complete oxidation of the monolayer of alcohol has been calculated from the constant rate of oxygen consumption as being 7.5 hr. Thus, the flattening actually marks the end of the photooxidation with much acetone remaining adsorbed.

This conclusion suggests that a knowledge of the adsorption of acetone on "hydrated surfaces" of TiO_2 is necessary to explain the evolution plots of acetone during photocatalysis. Assuming that all of the oxygen consumed during illumination is used in the photooxidation of isopropanol to yield acetone, the amount of acetone remaining adsorbed at different stages of the photocatalytic runs can be evaluated as the difference between the amount in the gas phase and the total amount produced, calculated from the rate of oxygen uptake. Table 1 was obtained in this way using data from Fig. 4a and the results have been plotted in Fig. 6a, giving a "linear isotherm" which does not extrapolate to the origin.

This result can be easily explained using adsorption data for water, isopropanol, and acetone published elsewhere (7). Those studies show that acetone can be adsorbed at 273 K on water and isopropanol-covered TiO_2 surfaces giving isotherms A/W and A/I in Fig. 6. Meanwhile, adsorbed acetone (A/W) cannot be completely removed by outgassing at 273 K, so that a second isotherm (A′/W) could be obtained giving the reversible adsorption at this temperature. The difference between these isotherms gives the irreversibly adsorbed acetone remaining on the hydrated surface (0.10×10^{-6} m^3 g^{-1}).

Going back to our linear isotherm (a) in Fig. 6 there are two important features which are worthy of note. Firstly, the "isotherm" does not extrapolate to the origin but to 0.03×10^{-6} m^3 g^{-1}. From isotherm A/I this is the acetone that must remain adsorbed on an isopropanol-covered surface in equilibrium with a very small pressure of acetone in the gas phase. This accounts for the induction period observed in the evolu-

TABLE 1

ACETONE ADSORBED AT DIFFERENT STAGES DURING THE PHOTOOXIDATION OF ISOPROPANOL (DATA FROM FIG. 4a)

Time (hr)	Acetone pressure (N m^{-2})	Acetone produced (N m^{-2})	Adsorbed acetone[a] ($\times 10^6$) (m^3 g^{-1})
1	6.5	69	0.04
3	32.0	206	0.11
5	64.5	345	0.18
7.5	84.0	520	0.27

[a] 100 N m^{-2} ≡ 6.34×10^{-8} m^3 g^{-1}.

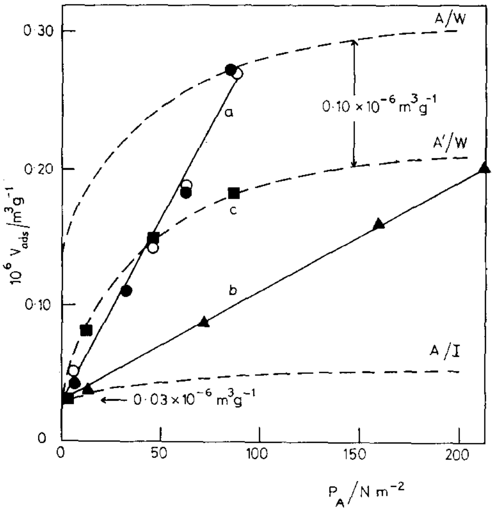

FIG. 6. Acetone adsorbed at different stages during the photooxidation of isopropanol as a function of the respective pressures of acetone in the reactor. (a), ● data calculated from Fig. 4a and in Table 1; (b), ▲ data calculated similarly from Fig. 4c; (c), ■ data calculated similarly from Fig. 5a. (○) Data from Table 2; (- -) isotherms of acetone adsorbed on water-covered (A/W and A′/W) and on isopropanol-covered (A/I) TiO_2 [from (7)].

tion plots for acetone. Now in order to produce 0.03 × 10^{-6} m^3 g^{-1} of acetone, ~10% of the isopropanol monolayer must be oxidized and one may directly calculate that this will occur after 45 min of illumination. Secondly, the coverage of acetone adsorbed on the sample after 7.5 hr of illumination, when all of the isopropanol has been oxidized and the surface covered with water molecules, is controlled by the isotherm A/W. Thus, we may conclude that after the start of illumination the surface, which initially holds isopropanol coordinatively adsorbed on the Ti^{4+} ions, becomes progressively covered by water molecules adsorbed in the same way, creating a surface covered with water and isopropanol on which the acetone is accommodated according to isotherms A/I and A/W, respectively. Data calculated on this assumption are shown in Table 2 and correspond well to the linear isotherm (a) in Fig. 6.

This model is also useful to explain the results of the photooxidation of isopropanol adsorbed on the hydrated surface shown in Fig. 5a. In this case a completely different evolution plot for acetone was observed, while water appeared in the gas phase. Adsorbed acetone in this experiment, calculated as in Table 1, corresponds to the isotherm A′/W, which refers to acetone weakly adsorbed on the hydrated surface. This suggests that now the water produced during photooxidation of the alcohol molecules adsorbed on the initially hydrated surface dislodges acetone from its strongest adsorption centers in this surface. Furthermore, comparing this result with those obtained using water in the gas phase and a surface covered with coordinatively adsorbed isopropanol, it may be concluded that only water produced *in situ* during the reaction is able to displace strongly adsorbed acetone from the hydrated surface, indicating a kinetic control of the displacement of acetone by water, as previously found (*7*).

Photooxidation of Isopropanol Vapor

In spite of the lack of any increase in the rate of consumption of oxygen, more acetone appears in the gas phase when isopropanol is in excess at the start of the experiments, as can be seen in Fig. 4b and c. The calculated amount of acetone remaining adsorbed during Expt (c) in Fig. 4 follows the linear isotherm (b) shown in Fig. 6. This isotherm extrapolates to the same value as isotherm (a) in the same figure and the amount of adsorbed acetone after 7.5 hr of illumination, obtained by extrapolation, corresponds to the isotherm A′/W of Fig. 6. All these facts suggest that the acetone, which is irreversibly adsorbed on the hydrated surface, is now being displaced by the gaseous isopropanol, leaving only weakly adsorbed acetone in equilibrium with the gas phase.

Calculations similar to those given in Table 2, but using isotherms A/I and A′/W, gave values for the acetone adsorbed during photocatalysis which correspond to the linear isotherm (b), confirming the assumption that in the presence of alcohol vapor the irreversibly adsorbed acetone on the hydrated surface is being displaced by alcohol molecules from the gas phase in a 1:1 molar ratio. The rate of consumption of alcohol gives the rate of such displacement, which is probably controlled by the rate of production of the tightly adsorbed acetone and, therefore, should be proportional to the over-

TABLE 2

ACETONE ADSORBED DURING EXPERIMENT SHOWN IN FIG. 4a CALCULATED FROM ISOTHERMS A/W AND A/I

Time (hr)	Acetone pressure (N m^{-2})	θ_W	θ_I	A on θ_W	A on θ_I	Total ads. A
				(× 10^6)(m^3 g^{-1})		
1	6.5	0.13	0.87	0.02	0.03	0.05
3.75	50.0	0.50	0.50	0.12	0.02_5	0.14_5
5	64.4	0.66	0.34	0.17	0.01_5	0.18_5
7.5	84.0	1.00	0.00	0.27	0.00	0.27

all rate of photooxidation and thus constant throughout the experiments.

It is now easy also to explain why isopropanol does not enhance the evolution of acetone from the hydrated surface. Data in Fig. 6b, together with the analysis of the irreversibly adsorbed species at the end of Expt (b) in Fig. 5, indicate that in this case the acetone is only reversibly adsorbed, as a result of the ability of the water produced *in situ* to dislodge the acetone from its strongest adsorption centers on the hydrated surface. Therefore, isopropanol vapor must be adsorbed on this surface, displacing the water molecules adsorbed in the place of acetone: thus the water pressure increases much more readily when isopropanol is present in the gas phase in the experiments of Fig. 5, although the acetone evolution does not increase as a result of alcohol adsorption. The similar rate of alcohol uptake from the gas phase on both dehydrated and hydrated TiO_2 surfaces (Figs. 4 and 5) suggests that the controlling step in the displacing process of acetone or water by isopropanol is actually the rate of oxidation of the adsorbed alcohol to produce the exchangeable species and not the displacement step itself.

Thus, in summary, it may be concluded that the evolution of acetone and isopropanol into the gas phase during photocatalysis is the result of a complex equilibrium between the species in the gas phase and on the surface, which is continuously modified by the progress of the photoreaction itself.

Photooxidation of Acetone

The description of the photooxidation of isopropanol has been based upon the assumption that acetone is not further oxidized during illumination under our experimental conditions. Bickley and Jayanty (*9*) have recently found using TPD-mass spectrometric techniques that formic acid appears on the surface of TiO_2 covered with isopropanol once all of the alcohol has been oxidized to acetone. Although this is probably the case for our sample outgassed at 325°C, a slow oxidation of the acetone strongly adsorbed on the hydrated surface must be assumed to explain the constant rate of oxygen consumption throughout the experiments.

In connection with this it is worthy of note that photooxidation of acetone coordinatively adsorbed on our sample occurs at a distinctly lower rate than that of isopropanol, suggesting that there is a kinetic control on this process, which apparently does not exist for the oxidation of the alcohol (quantum efficiency ~ 1). This could be explained by assuming that the easy removal of protons in the alcohol molecules readily produces alcoholate ions and $HO_2^{\cdot}$ according to Scheme A, while for acetone this step involves an activation energy barrier. Gravelle *et al.* (*6*) have shown that paraffins need photo-holes to be oxidized on TiO_2, probably to make possible the abstraction of a proton-like species. This would not be the case for isopropanol for which proton-like species are readily formed using the alcoholic hydrogen, but may be the mechanism for acetone oxidation, thus explaining the slowness of its photooxidation.

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