

## Heterogeneous Photocatalysis: *In Situ* Photoconductivity Study of TiO<sub>2</sub> during Oxidation of Isobutane into Acetone

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Received February 8, 1978; revised April 30, 1979

Using a special flow-reactor, the electrical photoconductivity  $\sigma$  of TiO<sub>2</sub> and the photocatalytic activity for isobutane oxidation at room temperature over this catalyst have been simultaneously measured. The formation rates in acetone (partial oxidation) and CO<sub>2</sub> (partial and total oxidation) as well as  $\sigma$  are proportional to light intensity, provided the photon energy is greater than the band gap of anatase. Kinetic orders have been determined. A reaction mechanism is suggested. In the pressure range from 100 to 500 Torr for O<sub>2</sub> and i-C<sub>4</sub>H<sub>10</sub> and under steady-state conditions, the electron-hole recombination is considered negligible; the dependence of  $\sigma$  upon  $P_{O_2}^{-1}$  is explained by the capture of photoproduced electrons by O<sub>2ads</sub> species in equilibrium with gaseous O<sub>2</sub>, whereas the independence of the formation rate in acetone upon  $P_{O_2}$  is interpreted by the neutralization and activation of O<sub>ads</sub><sup>-</sup> species (adsorbed at saturation) by photoproduced holes; isobutane reacts in a neutral adsorbed state with the activated oxygen species thus obtained.

### INTRODUCTION

The oxidizing properties of uv-irradiated TiO<sub>2</sub> are well known. If only organic compounds in gaseous or liquid phase are considered, several studies deal with the photocatalytic oxidation by O<sub>2</sub> over this solid at near-room temperature of alcohols (1-8), alkenes (9-11), alkanes (1, 9, 12, 13), and alkyltoluenes (14). It has been established that the primary step is the creation by photons of holes in the semiconductor valence band because of the excitation of electrons to the conduction band. Whether these holes react with negatively charged OH groups (2, 3, 5, 7, 15) and/or oxygen species of various types (2, 3, 5, 7-9, 15-18) has been disputed, as well as the nature of the activated species which react with the organic compound.

Since electrical charges are involved,

photoconductivity is a discriminating method to study the mechanism of photocatalytic oxidations over TiO<sub>2</sub>. Recently, kinetics (19) and photoconductivity (20) measurements have been independently carried out for the oxidation of gaseous isobutane chosen as a test reaction. However, the photoconductivity measurements were performed with pure gases and under much lower pressures than those used in the photocatalytic experiments. Therefore, it appeared of interest to design a flow-photoreactor which permitted simultaneous measurement of the photocatalytic activity and the photoconductivity of powder samples. This article reports the results obtained in the case of isobutane oxidation over uv-irradiated TiO<sub>2</sub>. These results are discussed in terms of the nature and role of the species involved in the elementary steps of the oxidizing attack of isobutane.

## EXPERIMENTAL

A differential flow-photoreactor was used at room temperature. The measurements were made under steady-state conditions to obtain reliable correlations between the simultaneous determinations of photocatalytic activity and photoconductivity. For electrical measurements, a frame ( $1.0 \times 1.5 \text{ cm}^2$ ) consisting of two gold electrodes maintained by two quartz bars was employed as a sample-holder in a reactor derived from the one described previously (9, 19). The catalyst was lightly compressed ( $3.3 \text{ kgf cm}^{-2}$ ) in this frame which was placed on a diaphragm whose aperture had the same dimensions as the solid pellet. This ensured that the stream of gas was forced to flow through the catalyst. The diaphragm and the reactor body were made of Teflon which is a good insulator even when water is present in the reaction products.

The catalyst was nonporous titania of  $70 \text{ m}^2 \text{ g}^{-1}$ , mainly crystallized in its anatase form, produced by Degussa (Frankfurt/Main). A single batch of the powder was calcined at  $653^\circ\text{K}$  in air for 48 hr to eliminate organic and inorganic (in particular  $\text{Cl}^-$  ion) impurities and then kept in a flask at room temperature. The amount required for each pellet was taken from this batch. Pure  $\text{O}_2$  was allowed to flow through the pellet at  $298^\circ\text{K}$  in the dark overnight. Then the reaction mixture was admitted and, after a few minutes, the uv illumination was switched on. Subsequently, the measurements were performed every 10 min and showed that a stationary state was reached after ca. 90 min of illumination for both photocatalytic activity and photoconductivity. In order to obtain another reaction mixture, the flow rate of one of the reactants was changed, while the total flow rate was kept constant by adjustment with the carrier gas (He).

The axis of the uv lamp (Philips HPK 125 W) was at ca. 6.5 cm above the catalyst layer. The ir fraction of the light was

eliminated by a water cell. The sample received ca.  $25 \text{ mW cm}^{-2}$  in the frequency range thus obtained.

The effluents were analyzed by gas chromatography. The electrical resistance of the catalyst was measured with a digital teraohmmeter (Guildline Instruments, Model 9520) using a 10 V dc voltage. Since the photoresistance varies only with the exposed area of the sample and is independent of the powder thickness under the present conditions (see next section), the photoconductivity is simply expressed by the photoconductance  $1/R$  in  $\Omega^{-1}$ .

## RESULTS

*Preliminary Remarks*

Intragranular diffusion of gas or vapor cannot occur since the anatase particles employed are nonporous. To make sure that external diffusion does not intervene, kinetic experiments have been performed with various flow rates. A flow rate ( $30 \text{ cm}^3 \text{ min}^{-1}$ ) equal to double the limit of the gas diffusion regime has been chosen. With such a flow rate and with partial pressures of reactants varying between 100 and 500 Torr, a low conversion level (ca. 1%) is obtained as required in a differential reactor.

The influence of the catalyst mass has also been examined. In a fixed-bed photoreactor, the catalytic activity varies linearly as a function of the mass below a certain critical value, corresponding to a completely uv-illuminated layer of catalyst, and becomes constant above it. In the present case, to make a convenient pellet we had to use a mass greater than the critical value in the sample-holder. However, it is possible to calculate the specific activity, since this value is known for the section of the pellet. For instance, the specific activity is equal to  $9.10^{-6} \text{ mol sec}^{-1} \text{ g}^{-1}$  for a mixture of 300 Torr of  $\text{O}_2$  and 300 Torr of isobutane. For brevity in the following sections, only relative

values, expressed by chromatographic peak heights, will be considered.

### Kinetic Orders

The following equation accounts for up to 95% of the isobutane transformation (19)



Small amounts of isobutanal and *tert*-butylalcohol are also formed. Partial oxidation is much more extensive than total oxidation.

Figure 1 shows the simultaneous variations in formation of acetone and CO<sub>2</sub> and in relative photoconductivity as a function of P<sub>O<sub>2</sub></sub>. For 100 and 200 Torr isobutane pressures, the curves have the same pattern. In the absence of oxygen, no acetone and CO<sub>2</sub> are detected. For P<sub>O<sub>2</sub></sub> increasing from 100 to 500 Torr, there is no significant change in the amount of

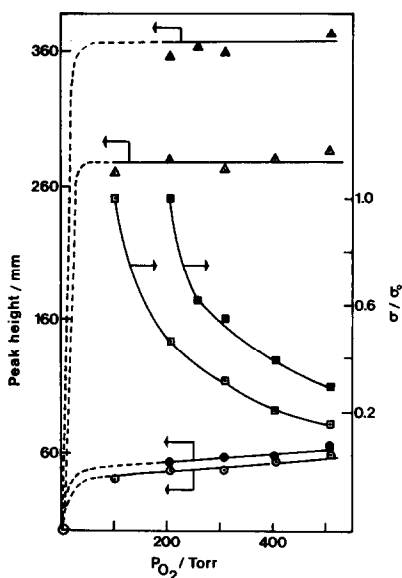


Fig. 1. Simultaneous variations in formation of acetone (triangles) and CO<sub>2</sub> (circles) and in relative photoconductivity  $\sigma/\sigma_0$  ( $\sigma = \sigma_0$  for initial O<sub>2</sub> pressure) as a function of oxygen pressure. Open symbols:  $P_{i\text{-C}_4\text{H}_{10}} = 100$  Torr; solid symbols,  $P_{i\text{-C}_4\text{H}_{10}} = 200$  Torr.

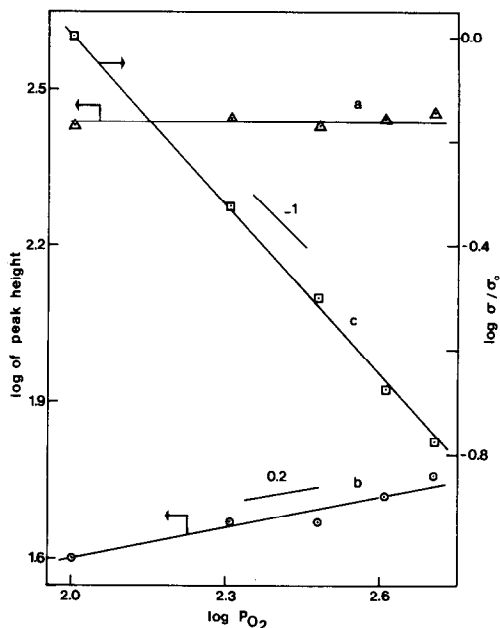


Fig. 2. Log-log plot of Fig. 1 curves for  $P_{i\text{-C}_4\text{H}_{10}} = 100$  Torr. Formation of (a) acetone, (b) CO<sub>2</sub>. Relative photoconductivity (c).

acetone produced, whereas a slight growth in the amount of CO<sub>2</sub> is observed. The relative photoconductivity decreases with increasing P<sub>O<sub>2</sub></sub>.

Figure 2 presents a log-log plot of the preceding curves for  $P_{i\text{-C}_4\text{H}_{10}} = 100$  Torr and P<sub>O<sub>2</sub></sub> varying from 100 to 500 Torr. The slopes of the straight lines obtained yield the kinetic orders with respect to O<sub>2</sub>. It may be seen that the rate in acetone is independent of P<sub>O<sub>2</sub></sub>, whereas the rate in CO<sub>2</sub> and the photoconductivity vary approximately as P<sub>O<sub>2</sub></sub><sup>0.2</sup> and P<sub>O<sub>2</sub></sub><sup>-1</sup>, respectively.

Figures 3 and 4 show the corresponding results as a function of isobutane pressure. The photoconductivity is not affected by  $P_{i\text{-C}_4\text{H}_{10}}$ . The kinetic order for acetone formation with respect to  $P_{i\text{-C}_4\text{H}_{10}}$  is close to 0.35 and does not change significantly for P<sub>O<sub>2</sub></sub> rising from 100 to 200 Torr, whereas that of CO<sub>2</sub> increases from 0 to 0.15.

The global orders for the photoconductivity as well as for acetone and CO<sub>2</sub> were also determined by changing the

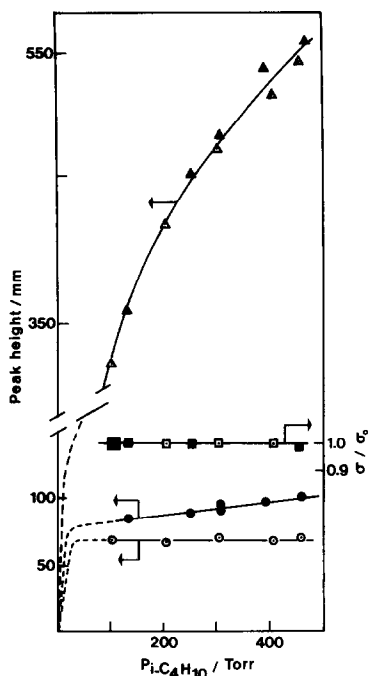


FIG. 3. Simultaneous variations in formation of acetone (triangles) and  $\text{CO}_2$  (circles) and in relative photoconductivity  $\sigma/\sigma_0$  ( $\sigma = \sigma_0$  for  $P_{i\text{-C}_4\text{H}_{10}} = 100$  Torr) as a function of isobutane pressure. Open symbols:  $P_{\text{O}_2} = 100$  Torr; solid symbols:  $P_{\text{O}_2} = 200$  Torr.

pressure of an equimolar mixture of  $\text{O}_2$  and  $i\text{-C}_4\text{H}_{10}$  between 200 and 600 Torr, while the flow rate was kept constant using a suitable He stream. They are in satisfactory agreement (less than 10% difference) with the sum of partial orders. This means that, in the pressure range used, each partial order is independent of the other reactant pressure. In other words, there is no adsorption competition between  $\text{O}_2$  and  $i\text{-C}_4\text{H}_{10}$  and no poisoning by the reactants and products.

Therefore, in the present experimental conditions, the photoconductivity ( $\sigma$ ) and the reaction rate in acetone ( $r_{\text{ac}}$ ) and in  $\text{CO}_2$  ( $r_{\text{CO}_2}$ ) are given by

$$\begin{aligned}\sigma &= k_{\sigma} P_{\text{O}_2}^{-1} P_{i\text{-C}_4\text{H}_{10}}^0 \\ r_{\text{ac}} &= k_{\text{ac}} P_{\text{O}_2}^0 P_{i\text{-C}_4\text{H}_{10}}^{0.35} \\ r_{\text{CO}_2} &= k_{\text{CO}_2} P_{\text{O}_2}^{0.2} P_{i\text{-C}_4\text{H}_{10}}^n\end{aligned}$$

with  $n$  increasing from 0 to 0.15 for  $P_{\text{O}_2}$  increasing from 100 to 200 Torr. Differences between  $r_{\text{ac}}$  and  $r_{\text{CO}_2}$  are not unexpected since  $\text{CO}_2$  is also formed by secondary reactions.

#### Light Intensity Influence

The intensity of the uv light was weakened by using various calibrated metallic grids, which does not change the energy distribution of the photons nor the geometry of the beam. Simultaneous measurements of the acetone and  $\text{CO}_2$  formation and of the photoconductivity showed that these quantities are proportional to the light intensity. The intensity  $I_0$  of the nonattenuated beam was weaker than the value corresponding to the saturation of absorption of  $\text{TiO}_2$ . In the plot of Fig. 5, expressed in reduced units, the experimental points are satisfactorily close to the first bisectrix.

#### Photon Energy Influence

Because of important loss in light intensity when employing a monochromator it was not possible in the present reactor to measure simultaneously the influence of the wavelength on the photoconductivity and the photocatalytic ac-

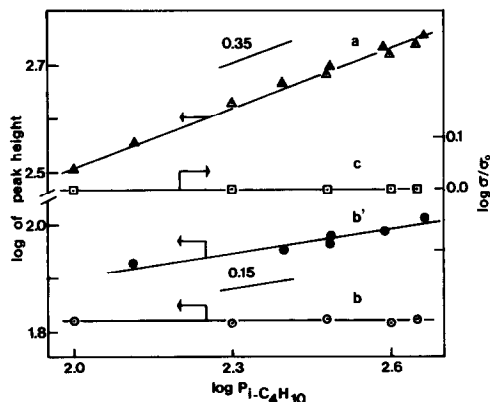


FIG. 4. Log-log plot of Fig. 3 curves for formation of (a) acetone, (b, b')  $\text{CO}_2$ . Relative photoconductivity (c). Open symbols:  $P_{\text{O}_2} = 100$  Torr; solid symbols:  $P_{\text{O}_2} = 200$  Torr.

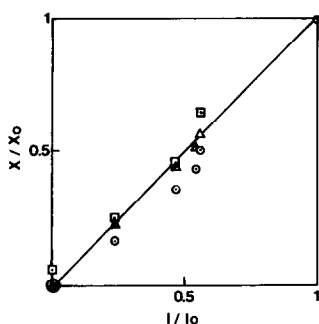


FIG. 5. Light intensity dependence of the photoconductivity (squares) and of the formation of acetone (triangles) and  $\text{CO}_2$  (circles) for  $P_{\text{O}_2} = P_{i\text{-C}_4\text{H}_{10}} = 200$  Torr. Reduced units: the subscript 0 refers to a nonattenuated beam.

tivity. However, independent measurements had been already performed using the same frame as in the present article for photoconductivity determinations in a static system (20) and a reactor presenting a greater uv-irradiated catalyst area for activity measurements (19). The data showed that the photoconductivity under a pure  $\text{O}_2$  atmosphere as well as the photocatalytic activity in acetone and  $\text{CO}_2$  were related to the photon energy according to a curve which corresponds to the absorption of uv light by anatase with an edge at ca. 3.2 eV.

#### DISCUSSION

Absorption of photons whose energy is greater than the band gap of anatase causes the excitation of an electron from the valence band into the conduction band, thus creating an electron-hole pair. In the dark, electrons already exist in the conduction band. Therefore, the main effect of uv illumination is, besides the production of additional conduction electrons, the creation of holes which behave as oxidizing agents. Both the proportionality of the reaction rate to light intensity and its dependence on photon energy which parallels the anatase absorption curve reflect the importance of the creation of electron-hole pairs for isobutane oxidation. The

electric field induced by surface negative charge density drives the photoproduced holes to the solid surface where they will react preferentially with negatively charged adsorbed species for electrostatic reasons.

Previous measurements (20) have shown that, unlike  $\text{O}_2$ , none of the carbonaceous compounds taking part in isobutane oxidation either as reactant or as products (i.e., isobutane, acetone, *tert*-butylalcohol, isobutanol,  $\text{CO}_2$ ) influences anatase photoconductivity  $\sigma$  when independently adsorbed, and also it has been shown that  $\text{H}_2\text{O}$  produces only a slight increase in  $\sigma$ . In other words, neither isobutane nor its products give rise to negatively charged adsorbed species. Consequently, only surface hydroxide ions and oxygen-adsorbed species carrying a negative charge can compete with electrons to combine with photoproduced holes.

#### Oxygen-Charged Species

ESR measurements have shown that  $\text{O}_2^-$ ,  $\text{O}^-$ , and  $\text{O}_3^-$  are the oxygen ions which most often exist on the surface of various oxides (21). For  $\text{TiO}_2$ ,  $\text{O}_2^-$  ion radicals have been detected after adsorption of  $\text{O}_2$  on reduced samples (21-24). They were also formed on unreduced samples illuminated (290-575 nm) in  $\text{O}_2$  at 298°K before scanning an ESR spectrum (23); their amount as a function of the illumination wavelength did not follow the  $\text{TiO}_2$  absorption curve. In addition, when anatase samples containing a small amount of  $\text{Ti}^{3+}$  ions were exposed to  $\text{O}_2$  at 298°K and uv irradiated at 77°K for 1 min, ESR signals, recorded at 77°K, were attributed to  $\text{O}_3^-$  and  $\text{O}_3^{3-}$  species (24). Nevertheless, the existence of  $\text{O}^-$  species on  $\text{TiO}_2$  cannot be ruled out on the basis of ESR measurements, since these species can be observed only in limited cases by this technique (25), as emphasized in an ESR study dealing with the adsorption of O atoms on  $\text{TiO}_2$  (26). ESR signal of  $\text{O}^-$  may be apparently absent in X-band

spectra and discernible in Q-band spectra recorded after removal of  $O_2^-$  species as recently reported for molybdena-alumina catalysts (27).

Electrical methods also yield information on charged oxygen species. Variations of the thermoelectronic work function have shown that two kinds of these species occur over unreduced anatase uv irradiated in 2 Torr  $O_2$  at 298°K (28). These species were tentatively identified as  $O_2^-$  ions and as oxygen atoms carrying approximately one negative charge. The photoconductivity  $\sigma$  of anatase outgassed at 423°K for 15 hr, then uv irradiated under vacuum at 298°K for 7 hr, was measured as a function of oxygen pressure  $P_{O_2}$  at room temperature (20). For increasing pressures (to 5 Torr)  $\sigma$  varied as  $P_{O_2}^{-1}$ , and, for decreasing pressures (from 5 Torr), first as  $P_{O_2}^{-1}$ , and then as  $P_{O_2}^{-1/2}$ . From these exponents it was inferred that, when  $P_{O_2}$  decreased,  $O_2^-$  species were first removed, then desorption of  $O^-$  species began; on the contrary, when  $P_{O_2}$  increased,  $O_2^-$  ions were the only species in equilibrium with the gas (20). We suggest that formation of  $O^-$  species occurred on introducing the first dose of  $O_2$  because of the existence of strong adsorption sites for oxygen, probably surface anionic vacancies. During photocatalytic experiments, the photoconductivity of  $TiO_2$  exposed to 100 to 500 Torr  $O_2$  and  $i-C_4H_{10}$  and to their reaction products varied as  $P_{O_2}^{-1}$ , which means that only  $O_2^-$  species were in equilibrium with gaseous  $O_2$ , while  $O^-$  ions saturated their adsorption sites under these pressure conditions.

In conclusion, the existence of  $O_2^-$  ions on uv-irradiated  $TiO_2$  appears unambiguous. On the basis of electrical measurements, we consider that  $O^-$  species also exist and saturate their sites under the photocatalytic conditions.  $O_3^{3-}$  ions were not observed on  $ZrO_2$  and  $SnO_2$  (24); since these oxides photocatalyze isobutane oxidation (30) and  $O_2$  isotopic exchange

according to the same mechanism as  $TiO_2$  (29), we conclude that  $O_3^{3-}$  ions are not involved in the present photocatalytic mechanism. Formation of  $O_3^-$  ions from  $O^-$  ions and  $O_{2ads}$  (21) competes with hole capture by  $O^-$  ions and with electron capture by  $O_{2ads}$ . With electrons and holes being constantly created under uv illumination, this formation is probably insignificant. Moreover, it depends upon oxygen pressure, unlike the present reaction rate. In summary,  $O_2^-$  and  $O^-$  ions are the only charged oxygen species which we shall consider for the mechanism of isobutane photocatalytic oxidation.

#### *Consideration on Hole Trapping by $OH^-$ Ions*

The linear dependence of oxygen photoadsorption upon the number of surface  $OH$  ions for  $TiO_2$  (31) has been attributed to hole trapping by these ions, which releases the associated photoproduced electrons to react with oxygen (2, 3, 15, 31). However, this does not rule out the reaction of holes with charged oxygen species, the population of which is equivalent to that of hydroxide ions under the present conditions of oxygen pressure, even in the case where all  $OH$  groups are supposed to carry a negative charge.

It has been suggested that  $OH$  radicals, produced on  $OH^-$  ions neutralization by holes, were required, together with  $O_2^-$  ions, for the photocatalytic oxidation of aliphatic alcohols over  $TiO_2$  (2, 3, 5, 7). The first attack of the alcohol molecule, which results in the abstraction of a hydrogen atom, may be due either to  $O_2^-$  (2, 3, 7) or to  $OH$  radicals (5). In the latter case,  $O_2^-$  was supposed to react with a water molecule (5). In both cases (2, 3, 5, 7) intermediate  $HO_2$  ions or radicals, as well as  $H_2O_2$ , were formed; however,  $H_2O_2$  decomposes under uv illumination (33).

If a similar mechanism were involved for isobutane oxidation, the participation

of  $O_2^-$  ions, in equilibrium with gaseous  $O_2$ , in the attack of isobutane molecules would imply a reaction rate proportional to  $P_{O_2}^{-1}$  in contrast with experimental results. On the other hand, we observed (34) that photocatalytic isotopic exchange of  $O_2$  occurred more rapidly over a partly dehydroxylated  $TiO_2$  (evacuation at 298°K, calcination at 723°K in  $O_2$  for 15 hr, evacuation at 423°K for 2 hr) than over a fully hydroxylated sample (evacuation under uv irradiation at 298°K for 15 hr). Since isobutane oxidation and  $O_2$  isotopic exchange require the same activation step for oxygen (35), we may conclude that a complete coverage in OH ions and  $H_2O$  molecules is not essential for isobutane photocatalytic oxidation.

For these reasons, we consider that neutralization of OH ions by photogenerated holes is not rate-determining for isobutane oxidation.

### *Proposed Mechanism*

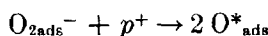
As  $TiO_2$  remains an n-type semiconductor during photocatalysis, its photoconductivity  $\sigma$  is proportional to the concentration of electrons. Consequently, as developed for uv- $TiO_2$ - $O_2$  interactions (20),  $\sigma$  must be proportional to the rate of formation of electron-hole pairs, i.e., to the incident flux of efficient photons as reflected in Fig. 5, and must parallel, when plotted against photon energy, the absorption curve of anatase. Photoproduced electrons can be trapped in various ways, specially by adsorbed oxygen species. The proportionality of  $\sigma$  to  $P_{O_2}^{-1}$  expresses that under steady-state conditions, the electrons are captured by  $O_{2ads}$  species in equilibrium with gaseous  $O_2$ ; if substantial electron capture by entities whose concentration does not depend on  $P_{O_2}$  to the first power were to occur, this proportionality would not be found. In particular electron-hole recombination should be negligible in regard to  $O_{2ads}^-$  formation.

In the following paragraphs, we shall only consider the formation rate in acetone. The kinetic orders for  $CO_2$  formation are difficult to interpret, since this compound is produced at the same time by partial and total oxidation reactions. The exponent 0.35 for isobutane pressure in the expression of the reaction rate for acetone indicates that isobutane reacts in the adsorbed state. As shown by photogravimetric measurements (34), isobutane coverage obeys the Langmuir law and, in the pressure range corresponding to the photocatalytic experiments, varies as  $P_{i-C_4H_{10}}^{0.3}$  in good agreement with the kinetic order. This alkane is adsorbed in a neutral form, since (i) no photoconductivity change was observed when varying its pressure during catalysis, which shows that it does not capture surface free electrons and corroborates earlier static measurements carried out in the absence of other adsorbates (20), and (ii) for electrostatic reasons, it seems unreasonable to assume that it would compete with negatively charged species to react with holes.

Assuming a Langmuir-Hinshelwood mechanism, the independence of the reaction rate in acetone upon  $P_{O_2}$  requires the concentration in the activated species which attack adsorbed isobutane not to be affected by  $P_{O_2}$ . On the other hand, these species should result from the interaction of negatively charged entities with holes, which, as already mentioned, are the oxidizing agents created by uv irradiation. Apart from  $OH^-$  ions,  $O^-$  species are the only species whose concentration is independent of  $P_{O_2}$  under photocatalytic conditions. On the basis of the arguments developed above, we suggest that activated species  $O_{ads}^*$  arise from the neutralization of  $O^-$  ions by holes. The existence of such species is supported by preceding data: oxygen isotopic exchange at near-room temperature over uv-irradiated  $TiO_2$  (35),  $SnO_2$ ,  $ZnO$ , and  $ZrO_2$  (29) involves a dissociated oxygen surface species which

also participates in isobutane photocatalytic oxidation as inferred from the comparison and competition between both reactions (35).

Moreover, since the present reaction rate is proportional to the concentration in holes, its independence upon  $P_{O_2}$  also implies that the consumption of holes by  $O_2^-$  ions, in equilibrium with gaseous  $O_2$ , is negligible in regard to hole capture by  $O^-$  ions. This is not unexpected since the reactivity of the superoxide ion is much less than that of  $O^-$  ion (21). Furthermore the attack of isobutane by undissociated oxygen species arising from the neutralization of  $O_2^-$  ions by holes has been ruled out in a preceding work (19) since (i) no hydroperoxide has been detected by gas chromatography during the photocatalytic oxidation of isobutane, and (ii) the decomposition of the isobutyl-hydroperoxide under the same conditions yields only small amounts of acetone and  $CO_2$ . On the other hand, the reaction

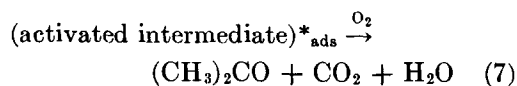
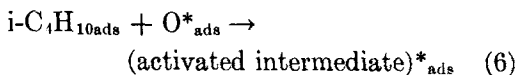
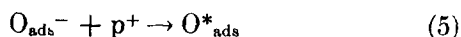
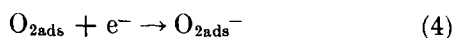
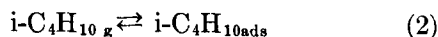
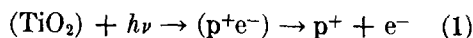


seems unlikely since oxygen dissociation would require more energy than that produced by charge neutralization.

It may also be noted that the absence of inhibition by the products indicates that they do not react with the activated oxygen species.

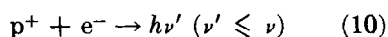
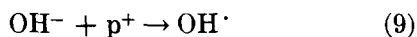
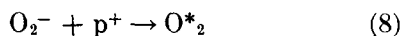
Finally, we suggest the following preponderant steps set out below: formation of electron-hole pairs (Eq. (1)); adsorption of the reactants (Eqs. (2) and (3)); electron capture by adsorbed oxygen (Eq. (4)); activation denoted by the asterisk of  $O^-$  ions through their neutralization by a photogenerated hole (Eq. (5)); attack of adsorbed isobutane by the resulting activated oxygen species (Eq. (6)); transformation of the activated intermediate obtained into the final products (Eq. (7)), which requires oxygen. The present results do not give direct information on this activated intermediate. As suggested (19),

it may be considered as activated *tert*-butylalcohol on the basis of the reaction of excited oxygen atoms with isobutane in gas phase (36). Since it is already activated, it is likely that the oxygen species which enables its transformation into acetone is not  $O^*_{ads}$ , but some sort of adsorbed oxygen which does not involve the participation of uv-created holes.



Experimental results yield no indication on the regeneration of  $O_{ads}^-$  species which are consumed in Eq. (5). It may involve dissociative adsorption of  $O_2$  or dissociation of superoxide ions which possess an additional electron in their antibonding orbitals.

On the contrary, we consider that the following equations



which correspond to hole capture by superoxide and hydroxide ions (Eqs. (8) and (9), respectively) are not preponderant, as well as electron-hole recombination (Eq. (10)) which would restore energy probably as light emission of a frequency either equal to that of incident irradiation for band to band recombination, or smaller when recombining centers intervene. In other words, the lifetime of electron-hole pairs is greater than the time required for a hole to meet and neutralize an  $O^-$  species.



Low photoconductivity values show that the surface is rather depleted of free electrons which are trapped by oxygen species.

Equations (5) and (6) indicate that at least one photogenerated hole is needed to transform one isobutane molecule, which means that the quantum yield  $\rho$  cannot be greater than 1. For photocatalytic isobutane oxidation over anatase,  $\rho$  has been found equal to  $\sim 1$  (9) or 0.1 (13). Similar values were measured for propan-2-ol oxidation at rutile surfaces either in liquid ( $\sim 0.4$ ) (5) or gaseous phase ( $\sim 1$ ) (2).

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