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PHOTOCATALYTIC OXYDATION MECHANISM OF ISOBUTANE
IN CONTACT WITH TITANIUM DIOXIDE (TiO_2)

M. Formenti, F. Juillet, S. J. Teichner

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1482 East Valley Road
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PHOTOCATALYTIC OXYDATION MECHANISM OF ISOBUTANE
IN CONTACT WITH TITANIUM DIOXIDE (TiO₂)

II. Reaction Mechanism

By M. Formenti, F. Juillet and S. J. Teichner

The photocatalytic oxidation of isobutane to acetone in the presence of ultraviolet irradiated titanium dioxide takes place in several steps, the first of which is the insertion of an oxygen atom onto the tertiary carbon transforming the isobutane into tert-butanol. This step implies the photonic formation of the O₂⁻ species and its reaction with positive holes. The tertiary butanol is then dehydrated to iso-butene which is oxidized acetone and carbon dioxide. Insertion of an oxygen atom onto the primary carbon leads to iso-butanal after oxidation of the alcohol. An analogous reaction scheme is proposed for all the alkanes.

Introduction

The photocatalytic oxidation of isobutane at ambient temperatures in the presence of titanium dioxide (anatase) irradiated by ultraviolet leads to a gradual and incomplete oxidation of this paraffin [1]. This reaction has been studied in the dynamic mode in a differential reactor described in a previous work [2,3]. The principal partial oxidation product is acetone, and also low quantities of isobutanal and tertiary butanol are formed. Carbon dioxide and water vapor arise essentially from the elimination of carbon

*Numbers in margin refer to foreign pagination.

from the aliphatic chain during the formation of acetone.

Generalization, under identical experimental conditions, of this heterogeneous photocatalytic process to normal and ramified alkanes has enabled us to transform them into a mixture of ketones and aldehydes [4,5]. The study of the reactivity of these paraffins has then shown that all the carbon atoms in the hydrocarbon chain are attacked and that the attack takes place preferentially on the carbon atom which has the most dense electron environment and the weakest steric effect. The following sequence of reactivities of the different types of carbon atoms has been determined [5]:

Tertiary C > quaternary C > secondary C > primary C

Gradual photocatalytic oxidation has been studied more closely by using isobutane as the reactant. The study of the reaction kinetics has been described in the previous article in this series [6] but purely kinetic data do not enable us to propose a detailed reaction mechanism. The study of intermediary compounds in the reaction, as well as data relative to the interaction with photons, prove to be indispensable to achieve this goal.

Also, it is necessary to briefly review the principal results, other than kinetic, obtained in the study of the oxidation of isobutane in contact with titanium dioxide illuminated by polychromatic ultraviolet radiation:

1. Only the irradiated portion of the catalyst is photoactive.
2. The photoactivity of titanium oxide relative to the oxygen-paraffin mixture disappears when the ultraviolet radiation is turned off, and it is reestablished when the irradiation is turned back on.
3. Only ultraviolet radiation ($\lambda < 3600 \text{ \AA}$) whose photons have energies greater than that of the band gap of TiO_2 (about 3.5 eV) is active in the catalytic photooxidation reaction [2,3,7].

4. The photocatalytic activity varies linearly with the irradiation intensity for low intensities. A saturation phenomenon is produced at too high an illumination.

5. It has also been shown by electron paramagnetic resonance that under ultraviolet irradiation titanium dioxide adsorbs oxygen at ambient temperatures in the form of O_2^- . In addition, all the photoactive solids noted, ZnO , ZrO_2 , SnO_2 [7], are capable of adsorbing oxygen in this form.

6. Temperature has little effect on the reaction rate [6]. The photocatalytic activity seems to depend only on the quantity of photoadsorbed oxygen [8].

7. The study of the reaction kinetics has shown that for the formation of acetone from isobutane, the reaction seems to proceed according to the steady-state oxygen adsorption mechanism (SSA model). A molecule of isobutane coming either from the gas phase or, rather, from the physisorbed phase forms an activated complex by reacting with an active oxygenated species adsorbed on the surface. This then proceeds to the formation of acetone.

It is, therefore, important to determine the nature of the reaction path between the attack of the hydrocarbon molecule by the adsorbed oxygenated species, and the final stage of the reaction, that is, the formation of the reaction products, principally acetone. This complex mechanism, which implies breaking and forming chemical bonds, should involve the simplest consecutive steps.

Results and Discussion

Reaction Mechanism of the Formation of Acetone.

In the photocatalytic oxidation of isobutane (stoichiometric mixture O_2 /isobutane = 2.5), isobutanal (selectivity 7%) arises from the attack of the hydrocarbon molecule at a methyl group (primary C) while the other oxidation products, acetone (selectivity 61%) and

tertiary butanol (selectivity 9%) result from the attack of the molecule at a tertiary carbon. The latter two compounds can arise from the oxidation of isobutane by two parallel reactions shown in diagram 1, but they can also result from consecutive reactions of isobutane into tertiary butanol into acetone. These two hypotheses are examined successively in the light of experimental results.

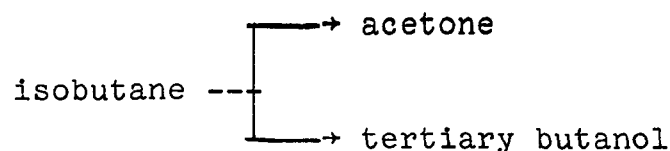


Diagram 1

In the case of the parallel reactions, acetone and tertiary butanol could result from the same intermediary compounds evolving along two reactive pathways. This hypothesis should explain the photochemical oxidation of alkanes in the liquid phase, that has been studied by different authors [9,10,11,12]. The case of the photochemical oxidation of cyclohexane, Stenberg, et al. [10], show that the first stage of this reaction is the formation of cyclohexyl hydroperoxide. This product is the precursor of the principal oxidation products, which are cyclohexanol and cyclohexanone. But in the case of the photo-oxidation of isobutane on TiO_2 , several experimental facts seem to show that the reaction does not proceed by way of a peroxide intermediary common to tertiary butanol and acetone.

This is how the ratio of the quantities of alcohol and ketone obtained in the photochemical oxidation reaction of cyclohexane is very different from that obtained in the present work for the photocatalytic activity of isobutane on TiO_2 . In effect, it has been shown that the quantities of tertiary butanol and acetone formed between 10 and 40°C vary inversely with respect to one another [6].

-- The hydroperoxide intermediary has not been detected by gas chromatography in the case of the photo-oxidation of isobutane.

-- The catalytic decomposition on TiO_2 of isobutane hydroperoxide under ultraviolet radiation in the presence or absence of

oxygen produces only small quantities of acetone and carbon dioxide. The presence of tertiary butylic alcohol has not been detected.

-- A radical reaction between isobutane hydroperoxide (tertiary butyle peroxide) and isobutane is not expected since no reaction takes place when this mixture is irradiated in the presence of TiO_2 .

It, therefore, seems that the possibility of peroxide or hydroperoxide intermediary should be excluded. Similarly, a chain radical reaction mechanism does not seem possible, since the use of a chain reaction inhibitor such as diphenylamine does not change the initial rate of reaction (it is, however, changed at the end of a certain period of operation of the reactor, since under these conditions the catalyst is covered by products resulting from the decomposition of diphenylamine).

It is, therefore, hardly probable that acetone and tertiary butanol would be formed according to the two parallel pathways in diagram 1. We have to consider, therefore, whether acetone results from the oxidation of tertiary butanol obtained from isobutane according to diagram 2.

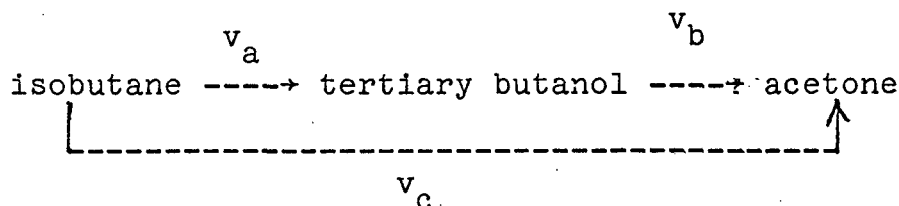


Diagram 2

The inverse variations in the quantities of tertiary butanol and acetone formed between -10 and $+40^{\circ}C$ are in agreement with this diagram.

To confirm its validity, we have to perform a comparative study of the photocatalytic oxidation of isobutane and tertiary butylic alcohol on titanium dioxide. The tests have been carried out under the same operating conditions at $25^{\circ}C$ with identical oxygen and reducing gas pressures and irradiation intensities [3]. The

oxidation of tertiary butanol produces acetone, carbon dioxide and water. The rate of formation of acetone (v_b), measured by the height of the acetone peak, is equal to the experimental errors close to the rate of formation of acetone from isobutane ($v_b \approx v_c$). It is therefore reaction (b) in diagram 2 which controls the kinetics of the photocatalytic oxidation of isobutane. But the rate of reaction v_a should be close to that of reaction v_b since the concentration of intermediary alcohol is low at 30°C (Fig. 3 in ref. [6]), but increases as the temperature decreases.

A study performed by infrared spectroscopy shows that tertiary butanol is adsorbed on TiO_2 in an irreversible manner. Spectrum b in Fig. 1 shows that the tertiary butanol is bound by hydrogen bonds (broad absorption peak between 3600 and 3100 cm^{-1}) and probably also in the form of alcoholate (band at 1620 cm^{-1}). UV radiation, in the absence of oxygen, in the gas phase, of this alcohol adsorbed on titanium oxide (same UV range as for the oxidation of isobutane) shows the formation of acetone adsorbed ($\nu=1680\text{ cm}^{-1}$) on acid sites (spectrum c in figure 1). The gradual appearance of adsorbed acetone bands is /1317 accompanied by a decrease in the transmittance of the TiO_2 pellet which shows that this oxide is reduced and that the surface lattice oxygen is capable of photo-oxidizing tertiary butanol into acetone. The irradiation of a mixture of alcohol and oxygen also produces adsorbed acetone ($\nu=1680\text{ cm}^{-1}$, spectrum d in figure 1), this time without changing the transmittance of the sample.

Therefore, from these results it seems that tertiary butanol is an intermediary photocatalytic oxidation product of isobutane on TiO_2 .

Comparison Between the Oxidation Mechanisms of Propane and of Isobutane.

In order to verify and generalize the hypothesis of an intermediary alcohol species, a comparative study has been carried out between the catalytic photo-oxidation of propane and isobutane. Propane is photo-oxidized in contact with TiO_2 mainly into acetone and CO_2 . It also forms low quantities of ethanal and isopropanal [4],

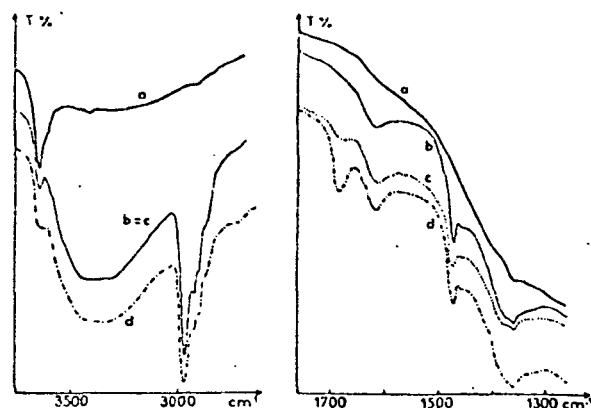


Figure 1. Infrared spectrum obtained during photo-oxidation of tertiary butanol.

- a) TiO_2 sample treated for 10 hours at 400°C under oxygen, then under vacuum at 25°C .
- b) TiO_2 exposed to alcohol, then under vacuum at 25°C .
- c) Irradiation of TiO_2 having previously adsorbed tertiary butanol.
- d) Irradiation of TiO_2 in the presence of a mixture of oxygen and tertiary butanol.

but no trace of isopropanol has been detected. However, under the same experimental conditions, isopropanol is photo-oxidized on TiO_2 into acetone.

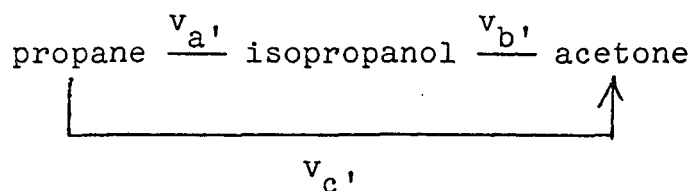


Diagram 3

Now, the rate of formation of acetone from alcohol (v'_b) is 30 times faster than that relative to the formation of acetone from propane ($v'_b \times 30v'_c$), which explains why the presence of intermediary alcohol has not been detected.

Under the same experimental conditions, the rate of oxidation of isopropanol into acetone is 50 times more rapid than that relative

to the oxidation of tertiary butanol into acetone. This result is logical since the oxidation of secondary alcohols is easy to obtain, while that of tertiary alcohols necessitates the use of powerful oxidizing agents.

In the case of a secondary alcohol such as isopropanol, its photocatalytic oxidation into acetone can be diagrammed in terms of a conventional direct oxidation mechanism. A nucleophilic agent (oxygenated species) attacks a hydrogen located at alpha in the hydroxyl group (diagram 4).

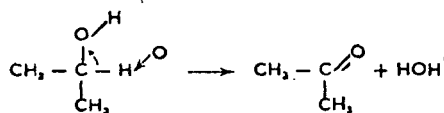
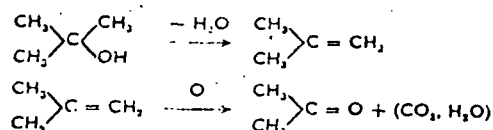


Diagram 4

Therefore, there is no difficulty in assuming that the propane is photo-oxidized into acetone by means of the formation of isopropanol.

This diagram cannot be applied to the oxidation of tertiary alcohols, since they do not possess hydrogen at alpha sites. From their high capacity for dehydration, they could, however, lose a molecule of water to give rise to an ethylene type of hydrocarbon, which could be oxidized into two kinds of carbonyl compounds (C=O bonds), aldehydes and ketones, if the double bond C=C is not terminal, and into a carbonyl compound (C=O bond) and carbon dioxide if the double bond is terminal:



This oxidation takes place in the presence of powerful oxidizing agents. The aldehydes thus formed can be oxidized up to the carbon dioxide and water stage. The intermediary formation of the olefin at the expense of tertiary butanol should, therefore, be considered.

It has been shown previously [2,3] that isobutylene is photo-oxidized on TiO_2 into acetone. A test carried out under the same experimental conditions shows that the rate of photocatalytic oxidation of isobutylene into acetone is slightly higher than that of tertiary butanol. The intermediary alkene, therefore, could not be detected. Like for tertiary butanol, the photocatalytic oxidation of isobutylene could be carried out by lattice oxygen in the absence of molecular oxygen. Ultraviolet irradiation of isobutylene adsorbed on TiO_2 (spectrum b in figure 2) leads to the onset of a band at 1680 cm^{-1} (spectrum c in figure 2) attributed to the carbonyl $\text{C}=\text{O}$ group in acetone.

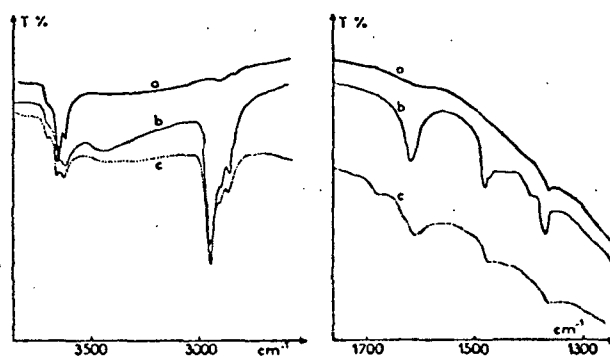
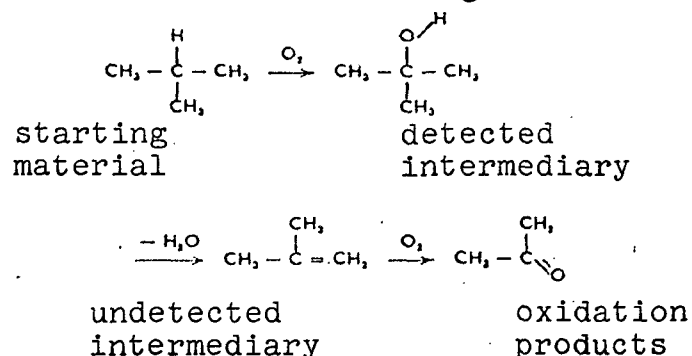


Figure 2. Infrared spectra taken during photo-oxidation of isobutylene.

- Sample of TiO_2 treated for 10 hours at 400°C under oxygen, then placed under vacuum at 25°C .
- TiO_2 exposed to isobutylene, then under vacuum at 25°C .
- TiO_2 irradiated in the presence of isobutylene adsorbed under oxygen in the gas phase.

The photocatalytic oxidation reaction of isobutane can, therefore, be diagrammed in terms of the following two reactions:

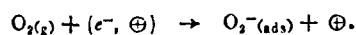


Photon Mechanism

It is, therefore, possible to consider that the first stage of the oxidation reaction of isobutane is the insertion of an oxygen atom on the tertiary C-H bond in order to form tertiary butanol, which then undergoes dehydration and oxidation to give rise to acetone. The insertion of oxygen on the primary carbon would lead to isobutanol, which would oxidize into isobutanal.

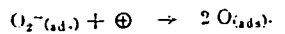
It has recently been shown [6,17] that isobutane has no interaction either with the UV radiation or with the solid. The ultraviolet photons absorbed by the solid should therefore activate the lattice or the gas phase oxygen, so that it could react with isobutane. It has previously been indicated that the atomic species O can insert on a C-H bond, forming tertiary butanol in the case of isobutane. The adsorbed oxygenated species O has not been detected, but its existence is not contradicted by the study of the reaction kinetics [6]. This species does not come from lattice oxygen, since infrared absorption studies have shown that isobutane exposed to TiO_2 under UV but in the absence of molecular oxygen does not undergo oxidation into acetone. On the other hand, tertiary butanol and isobutylene produce acetone under the same conditions. Thus, the initial stage of adding oxygen to isobutane should involve an oxygenated species other than that from the lattice.

A photon of suitable wavelength (of energy greater than the band gap of TiO_2 , $\lambda < 3600 \text{ \AA}$) absorbed at the surface of the oxide creates an electron-hole pair. A molecule of oxygen in the gas phase can be adsorbed as the O_2^- ion by freeing a positive hole according to the reaction:

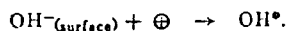


This $\text{O}_2^-(\text{ads})$ species is easily detected by EPR on samples of titanium oxide irradiated under oxygen by UV or even visible light [2,3], but only the $\text{O}_2^-(\text{ads})$ species formed in the presence of positive holes (hence for $\lambda < 3600 \text{ \AA}$) leads to the oxidation of isobutane.

The paramagnetic species O_2^- can, by recombining with the hole, dissociate from the adsorbed oxygen atoms, by the reaction



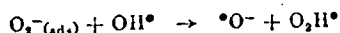
It has been suggested by Bickley, et al. [19] that the positive holes can be trapped by the OH^- ions on the surface of titanium dioxide:



The OH^\bullet radicals formed contribute, according to these authors, to the formation of dissociated oxygen:



or even



Regardless of the process selected, atomic oxygen could, therefore, be capable of attacking the C-H bonds of isobutane to give rise to tertiary butanol.

The overall reaction should account for the photo mechanism and for a chemical reaction mechanism with the formation of all the intermediaries. These results are summarized in Diagram 5.

If the formation of tertiary butanol requires the involvement of atomic oxygen, eventual oxidation of isobutylene into acetone becomes possible with lattice oxygen at the surface, as has been mentioned above. The reoxidation of the TiO_2 surface should similarly be possible with molecular oxygen [20].

According to Diagram 5, and assuming that atomic oxygen is involved only in the formation of alcohol, the photocatalytic oxidation of an isobutane molecule requires a half-molecule of photoactivated

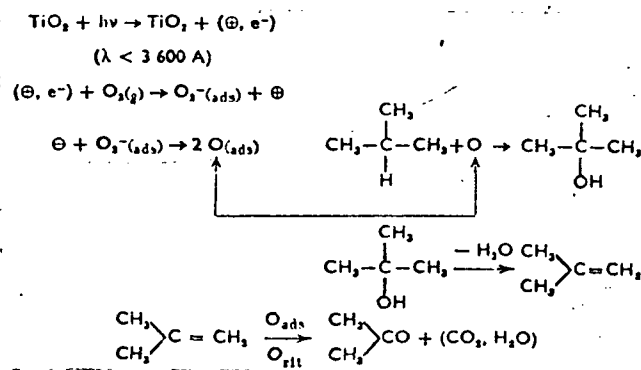


Diagram 5

oxygen (species O). The theoretical yield should therefore be equal to 2. If atomic oxygen, being very reactive, is also involved in the formation of the oxidation products of the alcohol, the result is a decrease in the quantum yield of the reaction.

In view of the selectivity with respect to acetone, and the reasoning above, the measured quantum yield should therefore be less than 2. In this work, the experimental quantum yield has been found to be equal to 1, when the number of photons is determined by calorimetry [7], but its actinometric determination [5] shows that it should be closer to 0.1.

Conclusions

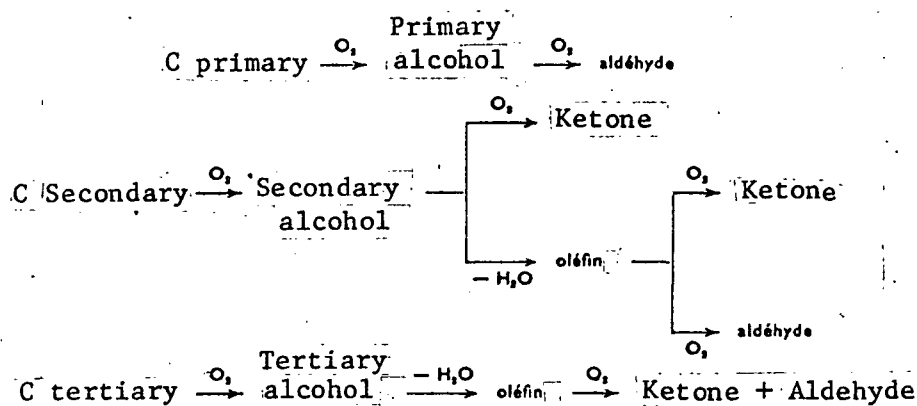
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The photocatalytic oxidation reaction mechanism of isobutane represented by the following sequence:

- insertion of an oxygen atom on the hydrocarbon chain in order to form tertiary alcohol;
- dehydration of the tertiary alcohol to produce isobutylene;
- oxidation of isobutylene into acetone;

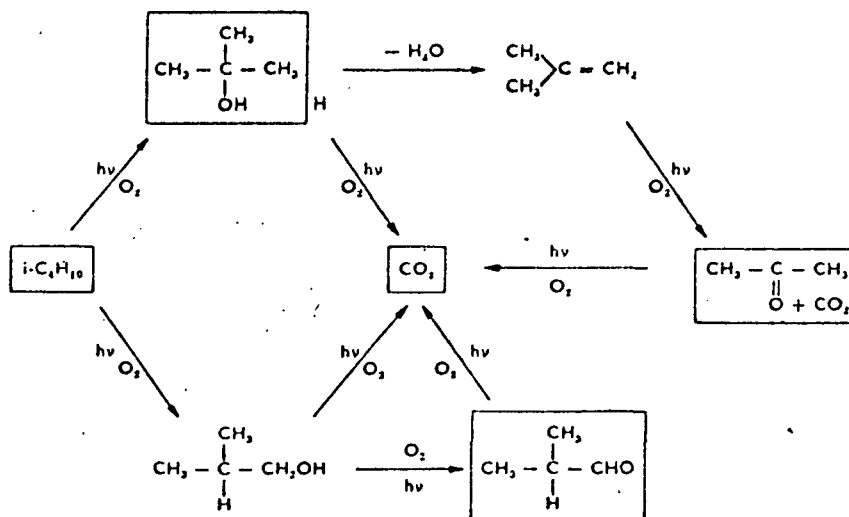
accounts well for the experimental results obtained in different studies carried out on this reaction. In particular, it explains the role of ultraviolet radiation and oxygen photo-adsorbed as O_2^- . Any solid

capable of photo-adsorbing oxygen at ambient temperatures in the form of O_2^- and having a band gap compatible with the energy of ultraviolet radiation (involvement of positive holes) should have a photocatalytic activity. The kinetic mechanism proposed (SSA model) is in agreement with the reaction scheme. In the steady state operation of the catalyst, only a small fraction of the surface is active [2]. This scheme could be generalized to other aliphatic hydrocarbons, whose photocatalytic oxidation has been studied by Djeghri [4,5]. For these hydrocarbons, the following reaction scheme is obtained:



A detailed study of the photo-oxidation of isopentane in contact with TiO_2 [18] undertaken recently is in agreement with this diagram.

In summary, the photocatalytic oxidation reaction system of isobutane can be diagrammed as follows:



The products in the boxes represent products identified and analyzed in the reactive mixture at the output of the reactor.

In contrast with photochemical oxidation of alkanes in the liquid phase by gaseous oxygen, the possibility of an intermediary hydroperoxide compound (ROOH) should be rejected. It seems that the first stage of the photocatalytic oxidation reaction of isobutane into acetone on TiO_2 is the formation of alcohol by the insertion of an oxygen atom on the C-H bond of a tertiary carbon.

The photocatalytic oxidation of paraffins seems to be possible only on solids capable of adsorbing oxygen in the form of O_2^- under UV irradiation. This condition is necessary but it is not sufficient. This species should be capable of reacting with a positive hole (created by UV irradiation if the band gap of the oxide so allows) to give rise to active atomic oxygen capable of realizing, within the first stage, its insertion into the paraffin to form an alcohol. The other stages in the reactive scheme (oxidation of the alcohol and the olefin formed by dehydration of the alcohol) could be realized by the same active species or by lattice or molecular oxygen activated by ultraviolet radiation.

The photocatalytic oxidation reaction can be summarized in the photochemical activation of an oxygenated species adsorbed on the solid and its interaction with paraffins, to give rise to the reaction products. These chemical reactions arise both from photochemistry (activation of the oxygen) and from catalysis (reaction in the adsorbed phase on the oxide surface).

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