

N78-11210

NASA TECHNICAL MEMORANDUM

NASA TM-75198

PHOTOCATALYTIC OXIDATION MECHANISM OF ALKANES
IN CONTACT WITH TITANIUM DIOXIDE

Translation of "Mécanisme de
l'oxydation photocatalytique
des alcanes au contact du
bioxyde de titane," Bulletin De La
Société Chimique De France, 1976, No. 7-8,
pp. 1032 - 1036

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National Aeronautics and Space Administration
Washington, D. C. 20546
September 1977

STANDARD TITLE PAGE

1. Report No. NASA TM-75198	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle PHOTOCATALYTIC OXIDATION MECHANISM OF ALKANES IN CONTACT WITH TITANIUM DIOXIDE		5. Report Date September 1977	
		6. Performing Organization Code	
7. Author(s)		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address SCITRAN 1482 East Valley Road Santa Barbara, California 93108		11. Contract or Grant No. NASW-2791	
		13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Mécanisme de l'oxydation photocatalytique des alcanes au contact du bioxyde de titane," Bulletin De La Société Chimique De France, 1976, No. 7-8, pp. 1032-1036			
16. Abstract			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 16	22.

NO. 195. - PHOTOCATALYTIC OXIDATION MECHANISM
OF ALKANES IN CONTACT WITH TITANIUM DIOXIDE.

1. KINETIC STUDY

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Abstract

Isobutane is photo-oxidized on TiO_2 (anatase) between -16 and $+180^\circ C$ in tertiary butanol and acetone. The formation of tertiary butanol precedes the formation of acetone. Above $20^\circ C$ the latter compound becomes clearly predominant. The reaction kinetics obey a steady state model of oxygen chemisorption with the involvement of isobutane in the physisorbed phase.

INTRODUCTION

We were the first to show that it is possible to oxidize isobutane [1,2] and other paraffins gradually [3,4] at ambient temperatures in the presence of oxide catalysts (essentially TiO_2) [5] irradiated by ultraviolet. Isobutane especially is oxidized over TiO_2 [5] in a mixture of acetone, tertiary butanol, isobutanal, carbon dioxide, and water vapor. Acetone is the principal product of the gradual oxidation. The selectivity for this compound can be as high as 95% [6]. The kinetics study described in this work relative to the rate of formation of this product is aimed at determining the partial orders of each of the reactants in the kinetics equation, and thus to gain access to the reaction mechanism.

RESULTS AND DISCUSSION

1. Effect of Reaction Temperature.

a) Apparatus.

It has been shown before that the photocatalytic activity of

*Numbers in margin refer to foreign pagination.

titanium dioxide in the gradual oxidation of isobutane disappears near 150°C [2,6]. The effect of temperature on the oxidation rate of isobutane has therefore been examined in the temperature range between -20 and $+180^{\circ}\text{C}$.

For the study of the reaction of temperatures higher than ambient (between 25 and 180°C), the reactor used is shown in the diagram in Fig. 1. It includes a heating device and an ultraviolet source. The lower part of the reactor is enclosed by a quartz plate by means of a device analogous to that of the upper part of the reactor, using O rings. The catalyst is deposited on a very fine mesh stainless steel sheet to allow a very highly uniform temperature in the reaction vessel. The catalyst is heated by means of an OSRAM lamp (15 v, 150w) [ref. 64635] mounted at the focus of a parabolic mirror. The amount of heating by the lamp enables us to adjust the temperature within the reactor. The flow rate of the gaseous reactants is 3 liters per hour.

In the temperature range between -20 and $+30^{\circ}\text{C}$, the reaction is carried out in a reactor connected to an external cryostat, cooled by the circulation of a glycol-methanol mixture.

b) Results.

In the temperature range between 30 and 180°C , the results are summarized by the curves in Fig. 2, which shows the change in the rate of formation of the reaction products (acetone and CO_2) as a function of temperature. Here, this rate is expressed directly by the chromatographic peaks of the acetone and the carbon dioxide. From the shape of these curves, we see that the rates of formation of the acetone and the carbon dioxide behave the same way, which tends to show that CO_2 comes from the oxidation of a carbon in the isobutane, while the rest of the molecule provides the acetone. Furthermore, the activity clearly decreases beginning at 80°C , and becomes zero near 180°C .

From about 110°C , the catalyst takes on a pink beige color, as has been noted before [6]. The coloration of the catalyst is deeper as the operating temperature of the catalyst is higher.

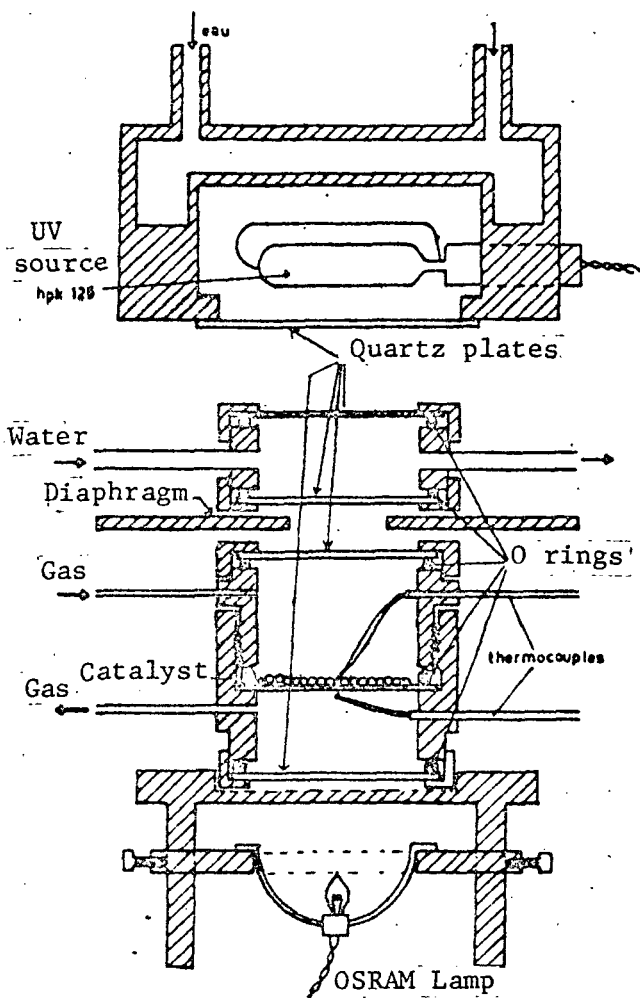


Fig. 1. Diagram of the Reactor

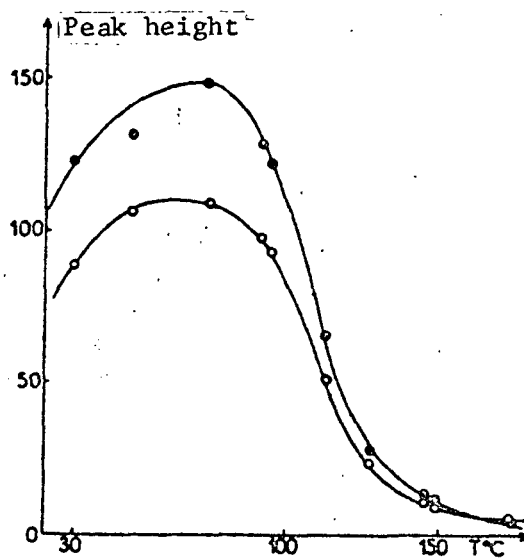


Fig. 2. The rate of reaction between 30 and 180°C.
 (● : acetone; ○ : CO₂).

At low temperatures (less than ambient) the behavior of the rates for the various oxidation products is reported in Fig. 3. The activity with respect to the formation of acetone decreases rapidly down to -10°C, a temperature at which it represents no more than 20% of the maximum activity.

In the dynamic range, under the experimental conditions used, it is not possible to measure these rates at temperatures less than -16°C. Errors can arise due to the condensation of water vapor. However, it has been shown by infrared spectroscopy that the bands of adsorbed acetone appear already at -50°C, from the photo-oxidation of isobutane, on titanium dioxide, in a static type reactor[7].

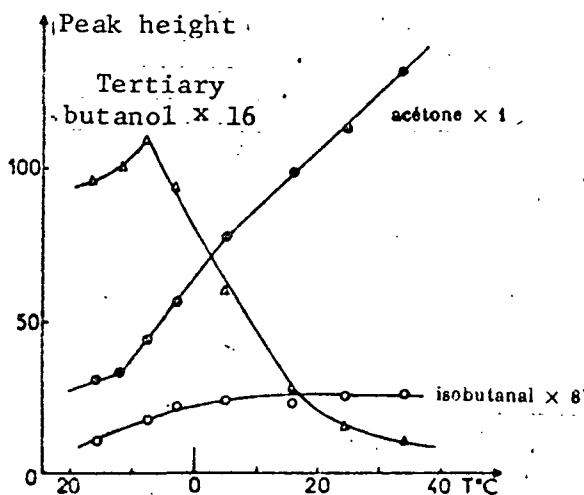


Fig. 3. Effective temperature (-20 to 30°C) on the rate of formation of various gradual oxidation products.

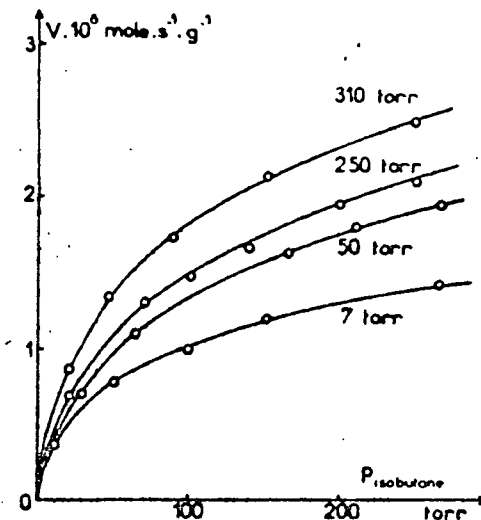


Fig. 4. Effect of isobutane pressure on the rate of formation of acetone for constant oxygen pressures.

The formation of carbon dioxide (not shown in Fig. 3) still shows the same changes as those of acetone. The formation of tertiary butanol increases greatly at low temperatures. The activity with respect to the formation of this compound is multiplied by a factor of 10 between 35 and -7°C, then the rate of its formation decreases slightly. We note that the temperature range in Fig. 3, the behavior of the rate of formation of acetone and of tertiary butanol are practically opposite, which seems to show that the formation of these products is related. Finally, above 0°C, the temperature has no influence on the formation of isobutanol.

c) Discussion.

From ambient temperature up to 50 to 60°C, the slight increase in the rate of formation of acetone (Fig. 2) can be attributed to an increase in the rate of desorption of these reaction products. This phenomenon is barely activated. The decrease in the activity for temperatures greater than 100°C can be due to the fact that the concentration of the paramagnetic O₂-species decreases, as this has already been shown [2]. These species practically disappear at 150°C, the temperature at which the rate of reaction is very low.

The coloration assumed by titanium oxide beginning at 110°C could be due to fragments fixed on the solid, resulting from the oxidation of isobutane by lattice oxygen, rather than by O₂⁻.

The sum of these results has to be reconciled with those obtained by Thevenet [8] in a study of the photocatalytic oxidation of carbon monoxide on TiO₂. This author found a reaction activation energy close to 3.1 Kcal per mole, in a temperature range between 30 and 110°C, and the participation of the lattice oxygen in the oxidation of CO. The work of Djeghri [3,4] on the photo-oxidation of alkanes in contact with TiO₂ shows that for propane the rate of formation of acetone increases with temperature below 50°C, and that it decreases for temperatures above 100°C. It remains constant for temperatures between 50 and 100°C. Similarly, in the study of the photocatalytic oxidation of ammonia, Mozzanega [9] has shown that between 60 and 120°C the photocatalytic activity remains fairly constant and that it decreases beginning at about 120°C. All these experiments on photocatalytic oxidation involving oxygen and a reducing gas (CO, alkane, or NH₃) therefore show an analogous behavior, and it is logical to assume that the fall in the photocatalytic activity is due to the decrease of the photoadsorbing power of the titanium oxide at these temperatures [2] and not to the nature of the photo-oxidized species. The inverse correlation between the rates of formation of acetone and tertiary butanol [3] enables us to predict that tertiary alcohol is the intermediary compound into which isobutane oxidizes, and which gives rise to acetone, a hypothesis which has subsequently been confirmed (see part 2).

2. Isothermal Study of the Reaction Kinetics.

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Before determining the reactive orders with respect to the different "partners" in the reaction, we have to review the data concerning the adsorption of reactants by titanium oxide, as well as the products obtained.

It has been shown previously that photo-adsorption of oxygen in the paramagnetic O₂ form takes place on titanium dioxide at ambient temperature in the presence of ultraviolet light [2,10,11]. An EPR

study of the reactivity of this adsorbed form with respect to isobutane has shown that ultraviolet irradiation is necessary for the O_2^- species to disappear by interacting with isobutane [2].

The adsorption of isobutane and the principal oxidation products (acetone, CO_2) on titanium dioxide has been studied by infrared spectroscopy [7].

At ambient temperature and in the absence of ultraviolet radiation, the adsorption of isobutane on TiO_2 , previously desorbed at $200^\circ C$, is completely reversible since subsequently isobutane is totally eliminated under vacuum. Probably this amounts to an essentially physical adsorption. Infrared spectra obtained in this study [7] showed the modification of the absorption bands of the hydroxyl groups of the anatase, caused by the adsorption of isobutane. The 3655 cm^{-1} band is shifted all the way to 3640 cm^{-1} . This shift corresponds to the formation of hydrogen bonds between the OH groups of the surface of the solid and the adsorbate. After eliminating the hydrocarbon phase, the 3640 cm^{-1} resumes its initial position at 3655 cm^{-1} . The interaction between isobutane and TiO_2 at ambient temperatures is therefore limited to the establishment of a weak hydrogen bond.

The effect of ultraviolet radiation at ambient temperatures on titanium dioxide revealed in the presence of isobutane leads to a decrease of the transmittance of infrared radiation, brought on by a partial reduction of the solid surface, which demonstrates the participation of the lattice oxygen, which, however, does not lead to acetone, since this species is not being detected. Acetone, adsorbed directly on titanium dioxide, is detected on the one hand by the formation of hydrogen bonds between the hydroxyl groups and acetone, and on the other hand, mainly by the 1610 cm band corresponding to the vibration mode of the CO group of the acetone adsorbed on the Lewis acid centers of the solid [12]. Reversible adsorption of carbon dioxide is detected in the form of bicarbonates fixed to the solid [13].

a) Effect of Isobutane Pressure.

The effect of the isobutane partial pressure on the rate of formation of acetone and carbon dioxide has been studied at 30°C in an isobutane pressure ranging between 20 to 300 torr, for various oxygen pressures. The results relative to the formation of acetone are summarized in Fig. 4 and show that the rate of this formation (in moles/sec/gram) increases with the isobutane pressure, and that consequently, for a given oxygen pressure, the order with respect to isobutane (the slope of the curves) is a function of the isobutane pressure. The reactive order is between 1 for low isobutane pressures and close to 0 for high pressures. The formation of CO₂ changes little as a function of isobutane pressure.

b) Effect of Oxygen Pressure.

An analogous study was undertaken by varying the oxygen pressure at constant isobutane pressure. The pressure range studied is between 10 and 250 torr of oxygen. The photon flux has been more intense (by about a factor of 1 to 2) in this series of experiments.

The results of the formation of acetone are summarized in Fig. 5. The rate of formation of this compound increases initially with the oxygen pressure in the range of low pressures of this gas, then tends to become constant for high pressures (approaches 0). However, it has been impossible to verify by linear transforms of these kinetic curves (see later on) if for low pressures the order with respect to oxygen is equal to 1 or to 0.5, which would indicate whether oxygen reacts in the molecular or the dissociated form.

c) Inhibition of the Reaction.

Secondary reaction products exert no influence on the rate of formation of the gradual oxidation products (acetone, isobutanol, tertiary butanol). In effect, no inhibition of acetone and of isobutanol is observed when the partial pressures of water (from zero to 20 torr) and of carbon dioxide (from zero to 22 torr) and of carbon dioxide (from zero to 200 torr) are introduced into the reactive circuit. Only the rate of formation of tertiary butanol is increased in the presence of water vapor.

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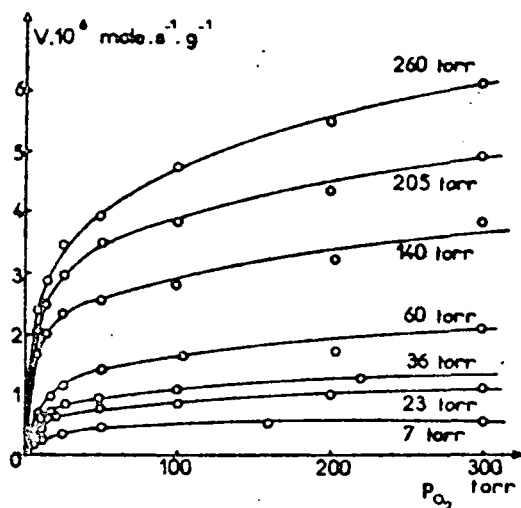


Fig. 5. Effect of oxygen pressure on the rate of formation of acetone for constant isobutane pressure.

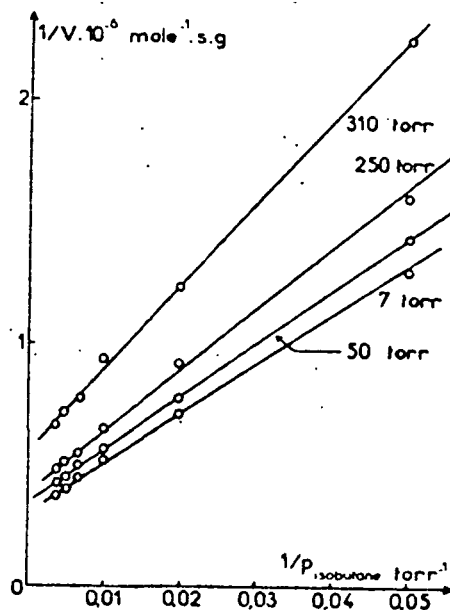


Fig. 6. Linear transforms representing the inverse of the rate of formation of acetone as a function of the inverse of the isobutane pressure for constant oxygen pressures (Fig. 4).

3. Reaction Mechanisms.

The kinetic curves relative to the rate of formation of acetone (Figs. 4, 5] are more easily interpreted by means of linear transforms, likely to lead to a mechanism compatible with other experimental data.

By expressing the inverse of the rate of formation of acetone as a function of the inverse of the isobutane pressure for different oxygen pressures (Fig. 4), we obtain a set of straight lines which are shown in Fig. 6.

For Fig. 5 we have been able to trace two types of transforms -- one where the inverse of the rate of formation is expressed as a function of the inverse of the oxygen pressure (Fig. 7) and one where this inverse is expressed as a function of the inverse of the square root of the oxygen pressure (Fig. 8).

The transform $1/v$ as a function of $1/p_{O_2}$ is a straight line for a wide range of pressures, but for high oxygen pressures linearity

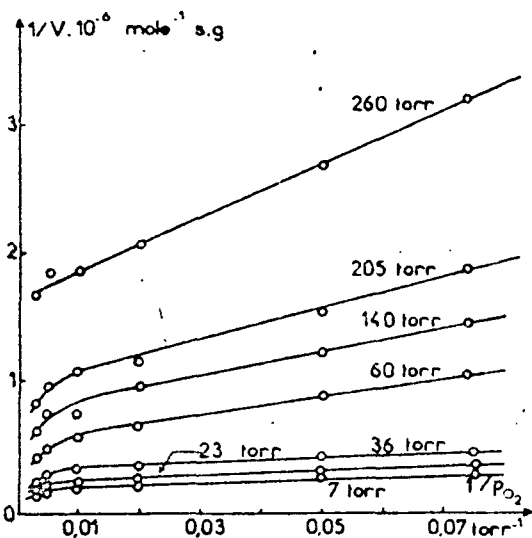


Fig. 7. Linear transforms representing the inverse of the rate of formation of acetone as a function of the inverse of the oxygen pressure for constant isobutane pressure.

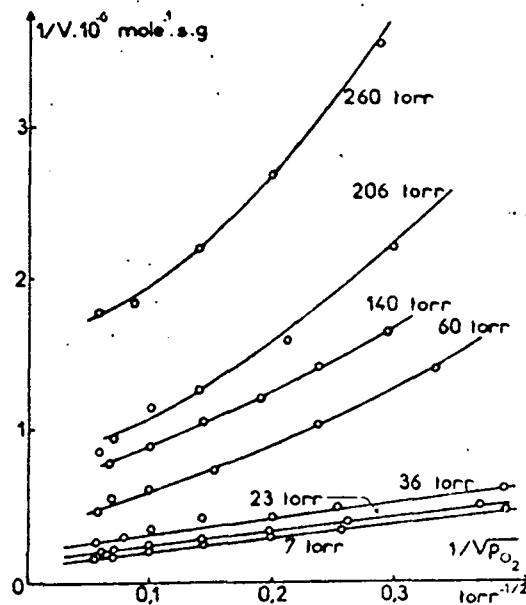


Fig. 8. Linear transforms representing the inverse of the rate of formation of acetone as a function of the inverse of the square root of the oxygen pressures for constant isobutane pressures (Fig. 5).

breaks down (Fig. 7). The linear transform $1/v$ as the function $1/\sqrt{p_{O_2}}$ leads to good results for low isobutane pressures, but the other lines are curved and the formula fits less well. Therefore, it seems like the $1/p = f(1/p_{O_2})$ transform would be better for the isobutane pressures despite the poorly fitting linearity for high values of oxygen pressure.

Three among the different reaction mechanisms likely to reflect the kinetic laws enable us to interpret the results obtained in a satisfactory manner. These are the Langmuir-Hinshelwood mechanisms, without concurrence of adsorption on the same type of sites, the oxidation-reduction mechanism proposed by Mars and Van Kravelen [14] and, finally, the mechanism of steady state absorption of the reactants, developed by Graydon, et al. [15-17] and nowadays known as the SSA model [18,19].

The Rideal or the Langmuir-Hinshelwood mechanisms with concurrence of absorption on the same type of sites are to be rejected since

they do not account for the experimental results.

Thus, we still have to determine which among the three mechanisms compatible with the kinetic results is the most probable.

The oxidation-reduction mechanism of Mars and Van Krevelen involving lattice oxygen could not represent all of the oxidation stages. In effect, lattice oxygen does not enable us to transform isobutane into acetone on TiO_2 , since it has been shown by infrared spectroscopy that in the absence of oxygen and in the presence of ultraviolet radiation, isobutane is not photo-oxidized into acetone. Only carboxylate /1035 species characterized by bands at 1550 and 1370 cm^{-1} are, therefore, detected by infrared spectroscopy. However, as has been shown in part 2, lattice oxygen could be involved in oxidation stages other than the first, which leads to the transformation of paraffin into alcohol.

The Langmuir-Hinshelwood mechanism should be rejected, since it has been shown by infrared spectroscopy [7] and by measurement of the work function of electrons from titanium dioxide exposed to ultraviolet radiation [10] that it produces no chemical adsorption of isobutane. Experimental conditions (reaction temperature, hydrocarbon pressure) enable us to assume that isobutane is physisorbed on the surface of the oxide ($T_e = 11.7^\circ\text{C}$ at 760 torr). If we assume that the physical adsorption of hydrocarbon at ambient temperature at pressure less than 300 torr obeys the Langmuir adsorption law, the steady state adsorption mechanism is represented by the equations

$$V_r = k_r \theta_{O_2} \frac{k_a P_{i_{100}}}{1 + k_a P_{i_{100}}}$$

$$V_o = k_o P_{O_2} (1 - \theta_{O_2})$$

where V_r represents the rate of reduction of the oxidized surface by adsorbing oxygen; V_o is the adsorption rate of oxygen at the surface; θ_{O_2} represents the rate of covering the surface by oxygen.

At steady state, the two rates above should be equal on the condition that the rate of oxygen desorption would be negligible compared with the rate of consumption of this reactant by the reaction:

$$V_o = V_r$$

therefore

$$k_r \frac{k_a P_{O_2}}{1 + k_a P_{O_2}} \theta_{O_2} = k_d P_{O_2} (1 - \theta_{O_2})$$

$$\theta_{O_2} = \frac{k_a P_{O_2} (1 + k_a P_{O_2})}{k_r k_a P_{O_2} + k_a P_{O_2} (1 + k_a P_{O_2})}$$

Therefore, the general expression for the rate becomes

$$V = \frac{k_r k_a k_d P_{O_2} P_{O_2}^2}{k_r k_a P_{O_2} + k_a P_{O_2} (1 + k_a P_{O_2})}$$

which gives the linear transform

$$1/V = 1/k_d P_{O_2}^2 + 1/k_r k_a P_{O_2} + 1. \quad [1]$$

The steady state mechanism (SSA model), which assumes the same type of linear transform as that of Mars and Van Krevelen, can therefore be applied with the reducing "partner" reacting in the physisorbed phase. The curves representing the inverse of the rate as a function of the inverse of the pressures of the two reactants effectively give straight lines (Figs. 6, 7).

The main hypotheses that are included in the Hinshelwood mechanism and re-examined by Graydon [21] are satisfied. In effect:

1) Oxygen is the chemisorbed species on the catalyst. It has been shown that titanium dioxide exposed to ultraviolet adsorbs oxygen. A part of this oxygen adsorbed in the form O_2^- is detected by electron paramagnetic resonance [1]. The other adsorbed forms are not directly identifiable.

2) The rate of oxygen desorption from the catalyst under vacuum is negligible. Ultraviolet irradiation under vacuum of titanium oxide containing O_2^- species formed previously produces negligible desorption of these species, and we obtain an equilibrium of stable absorption which defines a new state of the surface [1].

3) According to the hypothesis of Hinshelwood, for the reaction to take place according to the steady state adsorption mechanism (SSA model) the hydrocarbon molecule in the gas phase has to collide with an adsorbed oxygen atom. Now, under the experimental conditions of the reaction studied, it is more probable that the isobutane would react in the more condensed physisorbed phase and negligibly so in the gas phase. It, therefore, reacts in the non-activated state, as the SSA mechanism requires.

GENERAL CONCLUSIONS

The photocatalytic oxidation reaction of isobutane on titanium dioxide seems to proceed along a mechanism involving a steady state chemical adsorption of oxygen on the surface and a physical adsorption of isobutane. It seems to be difficult to specify if the oxygen reacts in the atomic form or in a molecular form, even though equation 1 seems to be better satisfied with the exponent $N=1$ (Fig. 7). Now acetone seems to come from tertiary butyl alcohol, since its disappearance, when the temperature rises (Fig. 3), is accompanied by the noticeable equivalent appearance of acetone. In the case where isobutane would produce acetone and tertiary butanol in two parallel and not consecutive reactions, such an inverse correlation would hardly be probable. It is shown in the second part of this work that tertiary butanol should become dehydrated under UV into isobutylene, which then oxidizes into acetone. However, the addition of molecular oxygen to isobutane leads to the formation of the hydroperoxide. Only the addition of atomic oxygen enables us to explain the formation of tertiary butanol [22,23]. Since above 20°C acetone clearly becomes the major product, the transformation of tertiary butanol into acetone should proceed easily, and the limiting stage would be the oxidation of isobutane into tertiary butanol. Since this reaction requires atomic oxygen, the exponent N in equation 1 should be equal to $1/2$, at least because the concentration of active atomic species depends on the oxygen pressure to the first power. This is possible if from one species of molecular oxygen such as O_2 - there is a formation into two atomic species [20], one of which leads to the oxidation of isobutane into tertiary butanol, and the other is used in the later (rapid) transformation of this alcohol into acetone.

The kinetic data alone do not enable us to propose a detailed reaction mechanism of the photocatalytic oxidation of isobutane on titanium dioxide. The secondary products of the gradual oxidation (tertiary butanol and isobutanol) should be involved in the reaction mechanism. The photo-oxidation rates of tertiary butanol and isobutylene into acetone should also be compared with those of the oxidation of isobutane. Finally, the photon mechanism, which implies the effect of the wavelength on the rate of gradual photo-oxidation, should be involved in explaining the role of anatase in the activation of oxygen.

The detailed mechanism of photocatalytic oxidation reaction of isobutane is thus described in the following article of this series. But it is possible to confirm even now that the photocatalytic activity is related to the presence of O_2^- species, even if these only play a precursor role.

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