

## Heterogeneous Photocatalysis: The Photooxidation of 2-Methylbutane

N. DJEGHRI AND S. J. TEICHNER

*Laboratoire de Thermodynamique et Cinétique Chimiques, L.A. No. 231 du CNRS, Université Claude Bernard Lyon I, 43, Boulevard du 11 Novembre 1918, 69621 Villeurbanne, France*

Received February 27, 1979; revised October 3, 1979

The mechanism of the photooxidation of alkanes implies an intermediate formation of alcohols and olefins which are then oxidized partially into ketones and aldehydes. When the corresponding primary alcohol (but not secondary or tertiary alcohols) and the corresponding olefins are photooxidized, the same reaction products are observed, but in addition, some products of a more intense oxidation are formed. In this last case the participation of adsorbed and uv-activated oxygen is supposed, whereas surface lattice, uv-activated, oxygen would be the agent of the milder oxidation of alkenes on the ethylenic bond, and of the primary alcohol, into aldehydes and ketones.

### INTRODUCTION

The partial oxidation of paraffins on titanium dioxide under uv irradiation at room temperature is one of the most studied examples of heterogeneous photocatalysis (1). The reaction products, mainly ketones and aldehydes, are formed through a sequence of steps including oxidation of the initial paraffin, dehydration into olefin of the alcohol formed in this first step or its further oxidation into ketone (for a secondary alcohol), and finally oxidation of the olefin into aldehyde and/or ketone (2, 3).

The oxidation agent is adsorbed (and dissociated) oxygen (atom or ion) (1) for some steps and lattice oxygen for others (4). Because of the complexity of this mechanism it was considered worthwhile to investigate thoroughly the photooxidation of 2-methylbutane and its various sequential intermediate products (various methylbutanol and methylbutenes) in order to ascertain the relative importance of each diverging step and determine the nature of the oxidizing species. Moreover, the growing interest in reactions influenced by light requires that all possibilities in the evolution toward various types of reaction products be investigated in order to evaluate the corresponding selectivities and side reac-

tions, if any. Indeed, if some desired products are favored in light-activated reactions the method of their preparation with the help of photons may be economically attractive.

### EXPERIMENTAL METHODS

The differential photocatalytic fixed bed reactor was described previously (5, 6). The effluents were analyzed by gas chromatography with helium used as a carrier gas. A mercury vapor lamp (Philips HKP 125 W) was used as a uv source whose infrared part was eliminated by a circulating water screen. The catalyst was a nonporous titania (97% anatase, 7% rutile) in the form of spherical particles of a mean diameter 200 Å, presenting a surface area of 67 m<sup>2</sup>/g, prepared by the flame reactor method (7). All reactants were of highest purity grade. The selectivity in reaction products  $S_c$  is related to the number of carbon atoms in these products (2).

### RESULTS AND DISCUSSION

#### A. Photocatalytic Oxidation of 2-Methylbutane

The composition of the mixture of reactants at atmospheric pressure was 20% alkane, 20% oxygen, and 60% helium. It has been shown previously that the total

conversion and the selectivities into reaction products depend on the composition of the feed (3, 6). Twenty milligrams of catalyst was uniformly spread on the porous membrane carrier in the reactor. This is greater than the critical mass above which photocatalytic activity is independent of the amount of catalyst (6). The flow rate of reactants ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) was in the range where the activity is still proportional to the contact time (0.6 sec) and where rate-determining intergranular diffusion is avoided. The overall conversion was of the order of 2% and the selectivities into various reaction products at  $30^\circ\text{C}$  are given in Table 1.

In what follows the selectivity  $S_c$  toward total oxidation ( $\text{CO}_2$ ) is always of the order of 15–17%. In general it depends on the ratio of organic compound/oxygen in the feed (6), but for various ratios the relative proportions of products of the partial oxidation remain practically the same (3).

The formation of ketones is favored in comparison with the formation of aldehydes, as for other alkanes (2). The presence of a tertiary carbon atom in the reactant accounts for a preferential formation of

TABLE 1

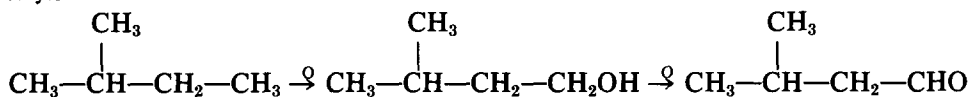
Selectivities for Reaction Products of the Photooxidation of 2-Methylbutane

Products	$S_c^a$ (%)	$S_c$ (%)
$\text{CO}_2$	15	—
Ethanal	16	19
2-Methylpropanal	5	6
3-Methylbutanal	5	6
Acetone	36	42
Butanone	12	14
3-Methylbutanone	10	12

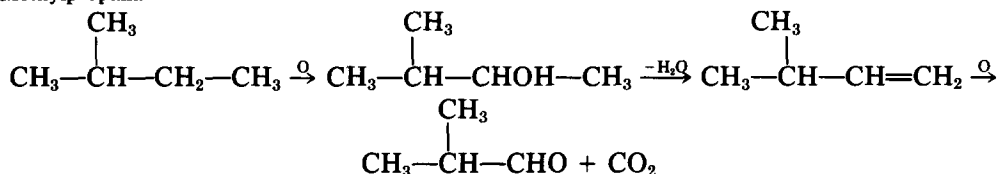
<sup>a</sup> Taking into account the selectivity toward total oxidation ( $\text{CO}_2$ ).

acetone (2). No alcohols were detected in the reaction products but it was shown previously that the first step is the formation of this intermediate whose dehydration or oxidation proceeds generally with a higher rate than its formation from alkane (2, 6). The general scheme for the formation of various products of Table 1 must involve oxygen atoms rather than molecules (2) and may be expressed (2, 3, 6) as follows:

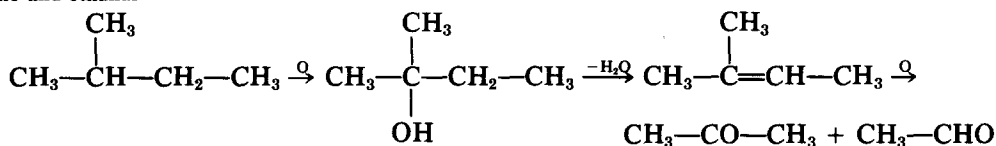
## 3-Methylbutanal



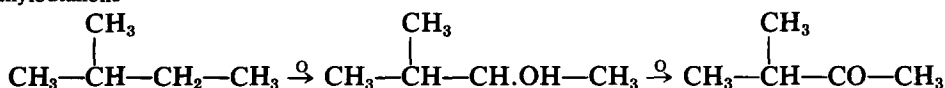
## 2-Methylpropanal



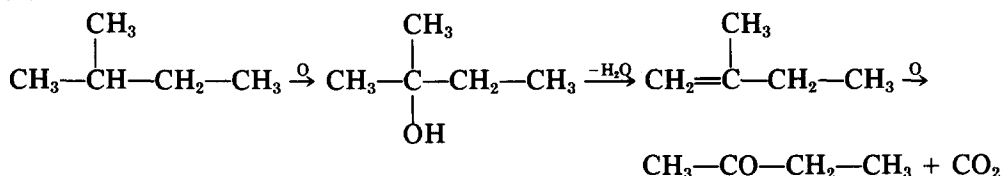
## Acetone and ethanal



## 3-Methylbutanone



Butanone



The formation of all the products may be explained, as before (2, 3, 6), by an initial formation of an alcohol, its direct oxidation into aldehyde or ketone, or its dehydration and a further oxidation of the generated olefin at the ethylenic bond. However, in order to investigate the possibility of side reactions which do not follow this scheme, the photooxidation of various methylbutanols and methylbutenes was performed under the same conditions as for the alkane.

### B. Photocatalytic Oxidation of Tertiary, Secondary, and Primary Methylbutanols

a. *2-Methyl-2-butanol*. Results are given in Table 2. It was shown before that under uv irradiation on  $\text{TiO}_2$ , even in the presence of oxygen, alcohols may be simply oxidized

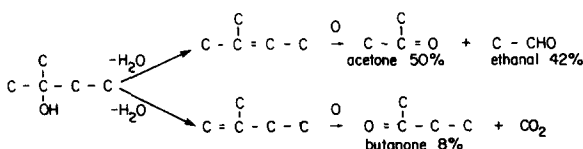
TABLE 2

Selectivities for Reaction Products of the Photooxidation of 2-Methyl-2-butanol

Products	$S_c$ (%)
Acetone	50
Ethanal	42
Butanone	8

into aldehydes or ketones or first dehydrated and then only oxidized (8).

In the photooxidation of a tertiary alcohol the first step should always be its dehydration into an olefin which is then oxidized. Indeed, tertiary alcohols are easily dehydrated, compared to secondary and primary alcohols. The following scheme therefore accounts for the reaction sequence:

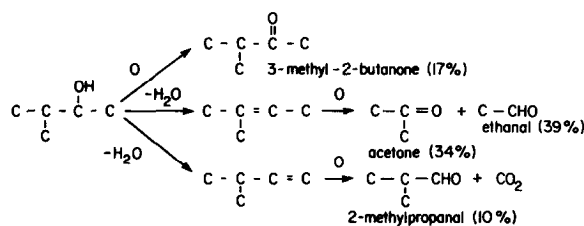


The ratio of selectivities into acetone and butanone shows that the dehydration of the tertiary alcohol leading to 2-methyl-2-butene (upper part of scheme) would proceed with a rate six times greater than the dehydration giving 2-methyl-1-butene (lower part of scheme). If ethanal is not obtained with the same selectivity as acetone it is because of its smaller stability toward oxidation, as compared with that of ketones (3). The olefins were not detected in the

reaction products, probably because of the facility of their oxidation (9), but their behavior as reagents in photooxidation is reported below.

b. *3-Methyl-2-butanol*. Results are given in Table 3. This secondary alcohol may be either directly oxidized into a ketone or first dehydrated into an olefin. 3-Methyl-2-butanone is the result of this direct oxidation (17%), whereas the dehydration as a first step gives two isomers: 2-methyl-2-butene

and 3-methyl-1-butene. The general scheme is therefore:



The results given in Table 3 show that the photodehydration proceeds almost three times faster than the direct oxidation of the secondary alcohol (into ketone). The dehydration itself proceeds faster with the elimination of hydrogen from the tertiary carbon (giving 2-methyl-2-butene) than from the primary carbon (giving 3-methyl-1-butene). Ethanal is obtained here with a selectivity higher than that of acetone. This behavior, which is the reverse of that observed previously for the photooxidation of the tertiary alcohol, giving by dehydration the same intermediate olefin (2-methyl-2-butene), was explained experimentally by the en-

hanced ability of ethanal to be photooxidized in the presence of the tertiary alcohol, in comparison to its reactivity in the presence of the secondary alcohol (3).

*c. 3-Methyl-1-butanol.* Results are given in Table 4. In a general way a primary alcohol is essentially oxidized into an aldehyde and its dehydration is difficult as compared with that of a secondary or a tertiary alcohol. The principal reaction product obtained here is 3-methylbutanal which is obtained by the direct photooxidation of the primary alcohol. The tentative scheme would be (two upper lines):

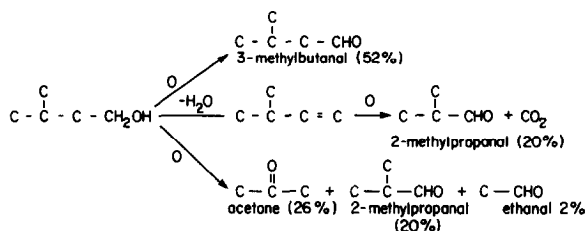


TABLE 3

Selectivities for Reaction Products of the Photooxidation of 3-Methyl-2-butanol

Products	$S_c$ (%)
Ethanal	39
Acetone	34
3-Methyl-2-butanone	17
2-Methylpropanal	10

TABLE 4

Selectivities for Reaction Products of the Photooxidation of 3-Methyl-1-butanol

Products	$S_c$ (%)
3-Methylbutanal	52
2-Methylpropanal	20
Acetone	26
Ethanal	2

However, the relatively high selectivity into 2-methylpropanal (20%) which would be obtained by the photooxidation of the intermediate dehydration product (3-methyl-1-butene) is difficult to account for by this sequence only as the dehydration of a primary alcohol is difficult. Besides, it would not explain the formation of acetone with a still higher selectivity (26%). Also the secondary possibility is that both aldehydes (2-methylpropanal and ethanal) as well as acetone come from the attack by oxygen on C-H bonds at tertiary, secondary, or primary carbons of the initial primary alcohol according to a mechanism similar to that observed for alkanes (2, 6) and described above. These products may also result from the oxidation of 3-methylbutanal (3) which is the major reaction product. The problem is reexamined below in relation with the photooxidation of 3-methyl-1-butene.

*d. Photodehydration of methylbutanols.* In the presence of oxygen olefins are not detected in the photocatalytic tests with tertiary, secondary, or primary methylbutanol. Also a test was performed under the same conditions as before but in the absence of oxygen. The feed was composed only of alcohol (20%) and helium (80%).

During the first minutes of the reaction small amounts of oxidation products are formed. However, this type of reaction rapidly ceases and the catalyst becomes blue, a color characteristic of (surface) reduced  $\text{TiO}_2$ . Only alkenes are then detected. In the case of the secondary alcohol (3-methyl-2-butanol) the ratio of the two possible olefins 2-methyl-1-butene/3-methyl-1-butene is equal to 2, in agreement with the selectivities toward the photooxidation products of this secondary alcohol (see above). When oxygen is introduced in the feed of reactants the catalyst recovers its white color whereas instead of olefins normal photooxidation products are detected. This behavior shows that during the first minutes of reaction the alcohol may be photooxidized either by adsorbed oxygen

or by oxygen from the surface lattice of  $\text{TiO}_2$  (9). If the dehydration products (olefins) are not detected during this first period this is because they are also oxidized by the same species. Indeed, olefins are also able to extract lattice surface oxygen from  $\text{TiO}_2$  giving a reduced (blue) solid. Once the catalyst is reduced on the surface to some extent, only the dehydration reaction can proceed and only olefins are detected. This type of reaction would normally proceed on acid sites, such as some titanium surface ions where the screening surface oxygen ions have been removed by reduction, or even Brønsted sites, as water is the product of reaction. This is confirmed by the inhibition of the reaction by traces of ammonia in the feed. The olefinic intermediates are not detected during the photooxidation of alcohols. They are formed only in the absence of oxygen (by photodehydration of alcohols). Also in order to investigate the last steps of the photooxidation reaction three olefins, 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene, were used as reactants under the same experimental conditions as before.

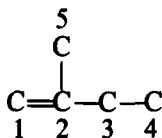
### C. Photocatalytic Oxidation of Methylbutenes

*a. 2-Methyl-1-butene.* The nature of products obtained (Table 5) shows that the reaction is not limited to an oxidation localized at the ethylenic bond which would give exclusively butanone. Butanone itself is only barely photooxidized in the same condi-

TABLE 5  
Selectivities for Reaction  
Products of the Photooxidation  
of 2-Methyl-1-butene

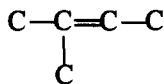
Products	$S_c$ (%)
Butanone	35
Ethanal	31
Acrolein	20
Acetone	11
Propylene oxide	3

tions, giving ethanal and acetone. This reaction product is therefore stable and the other products of oxidation in Table 5 must be formed directly from the 2-methyl-1-butene. If this molecule is designated as:



it appears that the rupture of the  $\text{C}_2-\text{C}_3$  bond would explain the previous results. The fragment  $\text{C}=\text{C}-\text{C}$  is compatible with the formation of acrolein and propylene oxide, whereas the fragment  $\text{C}-\text{C}$  is compatible with the formation of ethanal. Acetone may only be produced by the photooxidation of propylene oxide. Indeed, a direct photooxidation of this compound gives acetone (and  $\text{CO}_2$ ) whereas a direct photooxidation of acrolein gives only  $\text{CO}_2$ . These results may be compared with those of the photooxidation of propene where the following products are detected (10): propylene oxide, acrolein, acetone, ethanal (and  $\text{CO}_2$ ). Now, 2-methyl-1-butene should also be formed as an intermediate in the photooxidation of 2-methyl-2-butanol (see above), but only butanone results from its photooxidation. It appears therefore that the behavior of different hydrocarbons in the photooxidation depends on whether the compound is a sole reactant or whether it is also an intermediate reaction product formed on the surface.

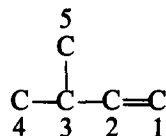
*b. 2-Methyl-2-butene.* As can be deduced from the simple formula:



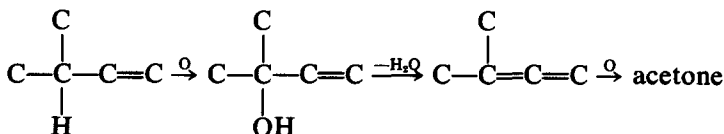
acetone and ethanal should be the main

products of photooxidation. However, as is seen from the results in Table 6, another unidentified product  $\text{P}_2$  is formed in an amount comparable to that of ethanal (31% by assuming that its gc retention time is that of 2-methyl propanal whose peak is very close). Although the identification of products  $\text{P}_2$  and  $\text{P}_3$  would have been very helpful for the comprehension of the mechanism of the photooxidation of olefins, the purpose of this work on alkanes is to show that some products of the photooxidation of alcohols are obtained through the photooxidation of olefins formed by photodehydration of alcohol. This is the case of acetone and ethanal (see above for the photooxidation of 2-methyl-2-butanol). Now, it is probable again that olefins used as sole gas reactants in the photooxidation have a different behavior that when formed as an intermediate species in adsorbed phase at low concentration. This is well demonstrated by the fact that products  $\text{P}_2$  and  $\text{P}_3$  are not detected during the photocatalytic oxidation of 2-methylbutane or 2-methyl-2-butanol.

*c. 3-Methyl-1-butene.* If the attack was localized on the ethylenic bond:



the reaction product would be only 2-methylpropanal. However, Table 7 shows that the major product of the reaction is acetone, whose formation supposes the rupture of the  $\text{C}_2-\text{C}_3$  bond. This rupture, already mentioned in the photooxidation of alcohols, can proceed, as for alkanes (9), by the insertion of oxygen in the  $\text{C}-\text{H}$  bond of the tertiary carbon of the olefin:



The enol formed in the first step is then dehydrated into allene which is oxidized into acetone. Indeed, an attempt at the direct photooxidation of enol (2-methyl-3-butene-2-ol) in the same experimental conditions showed very high reactivity of this compound giving 80% selectivity into acetone (no other products of partial oxidation detected). The simultaneous formation of acrolein and ethanal (Table 7) is explained as before in the case of 3-methyl-1-butanol by the oxygen attack on the C—H bond of methyl groups. This is quite probable, as shown by the results of the photooxidation of 2-methylbutane (formation of 3-methylbutanal, see above) and the previous results for other alkanes (2), all showing the formation of aldehydes on terminal CH<sub>3</sub> groups. It appears again here that the reaction products obtained in the photooxidation of alkenes employed as sole reactants come from an attack by oxygen at various points of the molecule, whereas when the alkene is an intermediate (through the dehydration of an alcohol) the main attack by oxygen concerns the ethylenic bond.

However, two types of oxygen species are involved in the photooxidation of alkenes, the surface lattice oxygen an ad-

sorbed oxygen, both activated by uv (4, 9). 3-Methyl-1-butene reduces the catalyst (which becomes blue) under uv irradiation, in the absence of oxygen. It reacts therefore with the surface lattice oxygen. The alkanes do not reduce the catalyst in the same conditions. They need adsorbed (and uv-activated) oxygen in order to be first transformed into alcohols (9). The alcohols, however, are oxidized by lattice oxygen (3). It is therefore quite possible that the formation of 2-methylpropanal from 3-methyl-1-butene involves a redox-type mechanism with lattice oxygen (1) whereas the formation of acetone requires adsorbed oxygen, according to the scheme above, including the intermediate formation of an alcohol. When the alkene is used as the sole reactant (high concentration) both reactions are observed, the formation of acetone being predominant (Table 7). But when this alkene is formed from the alcohol as an intermediate (low concentration) it reacts with a higher rate (9) with lattice oxygen (11) on the ethylenic bond giving 2-methylpropanal.

In conclusion, the following scheme for the photooxidation of alkanes (2-methylbutane) may be advanced:

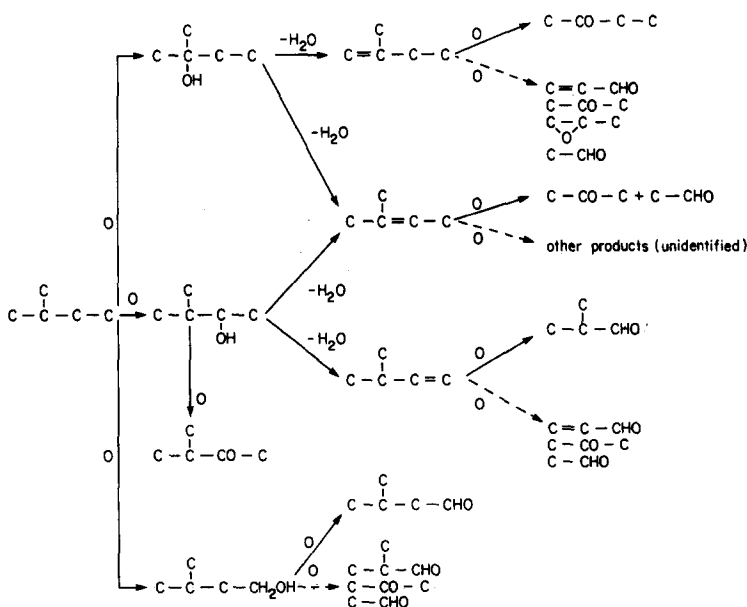


TABLE 6

Selectivities for Reaction Products of the Photooxidation of 2-Methyl-2-butene	
Products	$S_c$ (%)
Acetone	35
Ethanal	29
P <sub>2</sub> (unidentified)	31
P <sub>3</sub> (unidentified)	5

In the case of an alkane used as the sole reactant in the feed the sequence is that given by solid arrows. The first step is the formation of an alcohol from the C—H bond of tertiary, secondary, or primary carbon, giving 2-methyl-2 butanol, 3-methyl-2 butanol, or 3-methyl-1-butanol. These alcohols (primary and secondary) may be directly oxidized into corresponding aldehydes and ketones (solid arrows). However, when primary alcohol (3-methyl-1-butanol) is used as the sole reactant a further oxidation of other carbons of the molecule is observed giving other oxidation products (broken arrows).

A second possibility for secondary and tertiary alcohols formed from the alkane is their dehydration into various olefins (solid arrows) which are then oxidized on the ethylenic bond giving aldehydes and ketones (solid arrows). However, when an alkene is used as the sole reactant, in addition to the products formed from 2-methylbutane, other oxidation products are observed (broken arrows) which show that the attack by oxygen is not only limited to the ethylenic bond. Summing up, the behavior in the photooxidation of the primary alcohol (3-methyl-1-butanol) and of all the three alkenes is different when these com-

TABLE 7

Selectivities for Reaction Products of the Photooxidation of 3-Methyl-1-butene	
Products	$S_c$ (%)
Acetone	87
2-Methylpropanal	5
Acrolein	4
Ethanal	4

pounds are in high concentration (sole reactants) or in a nascent state formed as intermediates of the photooxidation of the alkane. In this last case the intermediate olefins are oxidized at the ethylenic bond.

## REFERENCES

- Formenti, M., and Teichner, S. J., in "Catalysis, Vol. 2, Specialist Periodical Report," p. 87, Chemical Society of London Edition, London, 1979.
- Djehri, N., Formenti, M., Juillet, F., and Teichner, S. J., *Faraday Disc. Chem. Soc.* **58**, 185 (1974).
- Walker, A., Formenti, M., Meriaudeau, P., and Teichner, S. J., *J. Catal.* **50**, 237 (1977).
- Kaliaguine, S. L., Shelimov, B. N., and Kazansky, V. B., *J. Catal.* **55**, 384 (1978).
- Formenti, M., Juillet, F., Meriaudeau, P., and Teichner, S. J., *Chem. Technol.* **1**, 680 (1971).
- Formenti, M., Juillet, F., Meriaudeau, P., and Teichner, S. J., in "Proceedings 5th International Congress on Catalysis (Florida 1972)" p. 1011. North-Holland American-Elsevier, 1973.
- Juillet, F., Lecomte, F., Mozzanega, H., Teichner, S. J., Thevenet, A., and Vergnon, P., *Faraday Disc. Chem. Soc.* **7**, 57 (1973).
- Cunningham, J., and Meriaudeau, P., *J. Chem. Soc. Faraday Trans. 1* **72**, 1499 (1976).
- Formenti, M., Juillet, F., and Teichner, S. J., *Bull. Soc. Chim. France* 1031, 1315 (1976).
- Disdier, J., Herrmann, J. M., and Pichat, P., Private communication.
- Thevenet, A., Juillet, F., and Teichner, S. J., *Japan J. Appl. Phys. Suppl.* **2**, 529 (1974).