

## Oxygen Effect on Photocatalytic Reaction of Ethanol over Some Titanium Dioxide Photocatalysts

KOZO ISEDA

Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462  
(Received September 25, 1990)

The suspensions of four kinds of  $\text{TiO}_2$  photocatalysts in ethanol have been studied under ultraviolet light in an atmosphere of Ar, air, or  $\text{O}_2$  at 25 °C. The main products were acetaldehyde, acetaldehyde diethyl acetal (acetal), acetic acid, water, ethylene, methane, carbon dioxide, and hydrogen. Acetaldehyde and acetal were abundantly produced in all of the products. The formation of all of the products under  $\text{O}_2$  was more efficient than those under Ar and air. The photochemical activity of each  $\text{TiO}_2$  is stronger than that of either  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}$ .

Photocatalytic  $\text{H}_2$  evolution from ethanol over  $\text{Pt}/\text{TiO}_2$  catalysts has frequently been reported;<sup>1–6)</sup>  $\text{CH}_3\text{CHO}$ ,<sup>1,2,4,5)</sup> acetal,<sup>2)</sup> and acetic acid<sup>1)</sup> are major photocatalytic products. However, no instance has yet been reported concerning a quantitative photocatalytic formation on all products from ethanol using various  $\text{TiO}_2$  catalysts.

Because the catalytic activity of  $\text{TiO}_2$  is presumed to be caused by active oxygen liberated from  $\text{TiO}_2$ ,<sup>7)</sup> the activity is decreased by a reduction of the catalyst, itself, due to light illumination;<sup>7)</sup> no report, however, has demonstrated the influence of such a decrease in the activity on all products from ethanol, except that regarding the evolution of  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  by the author.<sup>8)</sup> To determine the catalytic activity of  $\text{TiO}_2$ , itself, becomes difficult if Pt is deposited on  $\text{TiO}_2$ , since the reduction of  $\text{TiO}_2$  is depressed by Pt.<sup>9)</sup> Therefore, this work was undertaken with only  $\text{TiO}_2$ , without Pt, and studied in detail regarding effects due to the reactivation of  $\text{TiO}_2$  with  $\text{O}_2$  on all of the products formed from  $\text{C}_2\text{H}_5\text{OH}$  by a comparison of the results from blank tests under Ar, air, or  $\text{O}_2$  atmospheres, and that with the  $\text{TiO}_2$  under each atmosphere. Furthermore, a comparison was made with that involving  $\text{TiO}_2$  as well as  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}$ .

### Experimental

**Photocatalysts.** The  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ , and  $\text{TiO}$  used were the same as that described previously.<sup>8)</sup> Commercial  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}$  used were 99.9%, 300 mesh, Furuuchi Chemical Co., Ltd., respectively.

**Ethanol.** In the same manner as described in a previous paper,<sup>8)</sup> the commercial  $\text{C}_2\text{H}_5\text{OH}$  (99.5%, special grade, Katayama Chemical Co., Ltd.) used was purified by distillation after drying over  $\text{CaO}$ .

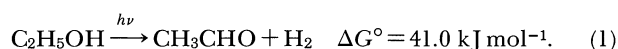
**Reaction Procedure.** The experimental conditions were similar to those published previously.<sup>8)</sup> The water tank used was a Riko RH400-10W photochemical reactor. After illumination, the reaction tube was immediately transferred to a beaker containing ice-water and was kept for about 15 min in a refrigerator. This is because the  $\text{CH}_3\text{CHO}$  produced should be kept in the dark while in the liquid-phase as much as possible. A blank test for a mixture of

$\text{CH}_3\text{CHO}$  (0.2 ml) and  $\text{H}_2\text{O}$  (1.8 ml) or that of  $\text{CH}_3\text{CHO}$  (0.2 ml) and  $\text{C}_2\text{H}_5\text{OH}$  (1.8 ml) was carried out under an Ar atmosphere without any catalyst in a similar manner as in a previous study.<sup>10)</sup>

**Analysis.** The analytical conditions were also similar to those run in a previous study.<sup>8)</sup> A Shimadzu GC-8A gas chromatograph (activated charcoal, 60–80 mesh) was used for the analysis of gaseous products. All liquid products, except for acetic acid, were analyzed using a Shimadzu GC-4B gas chromatograph (PEG-6000 10%, Flusin P, 30–60 mesh). Subsequently, acetic acid was analyzed by a Perkin-Elmer 900 gas chromatograph (PEG-6000 10%, Flusin P, 30–60 mesh, 2 mm $\phi$ ×1.8 m glass column, 140 °C,  $\text{N}_2$  carrier, FID). In this experiment, the yields of all products with  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ , and  $\text{TiO}$  include that of a blank test under each atmosphere (Figs. 1, 2, and 10).

### Results and Discussion

Figures 1 and 2 show the formation of liquid products and that of gaseous products from ethanol versus the illumination time observed for a blank test under an Ar or air atmosphere, respectively. Because  $\text{CH}_3\text{CHO}$  and  $\text{H}_2$  are produced during the initial illumination, the first reaction of ethanol proceeds as follows:<sup>1)</sup>



This result is particularly important in view of the fact that ethanol fails to undergo any reaction; this is because of its absorption maximum at 174 nm<sup>11)</sup> under UV light, since Pyrex glass does not pass UV light below about 230 nm. The cause of the reaction described in Eq. 1 is most likely to be due to slight substances having photosensitive action dissolved in ethanol from the natural rubber liner; natural rubber usually contains small amounts of other additive impurities. Once  $\text{CH}_3\text{CHO}$  forms, it serves as a sensitizer, since it has an absorption maximum at 293 nm<sup>12)</sup> in its ultraviolet spectrum, and Pyrex glass passes about 40% of the UV light at a wavelength of 290 nm. Accordingly, some of the products shown in Figs. 1 and 2 were slightly produced without  $\text{TiO}_2$ . Acetal and  $\text{CH}_3\text{COOH}$  were not detected at for illumi-

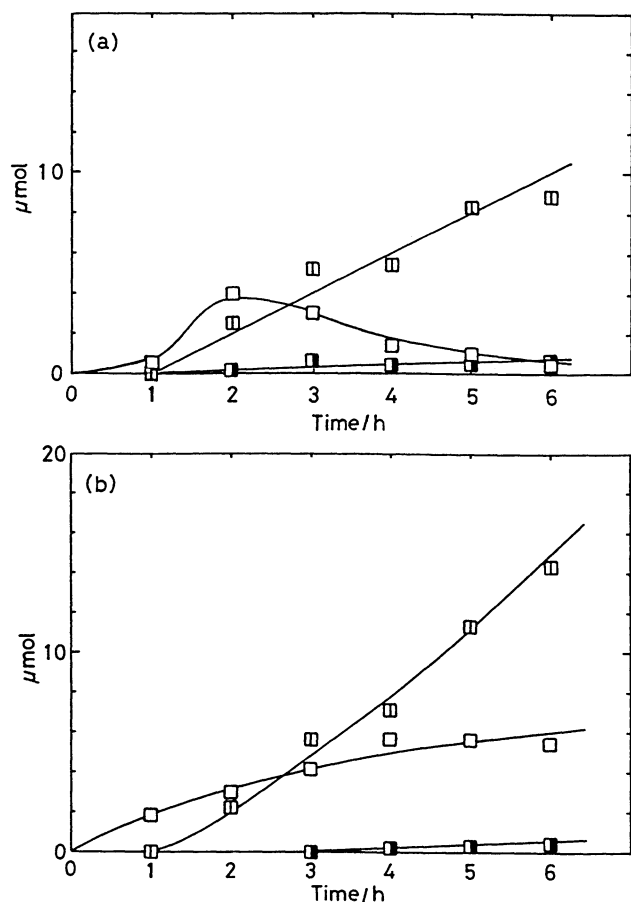


Fig. 1. Formation of liquid products from 2.0 ml ethanol vs. illumination time for a blank test without any TiO<sub>2</sub> under Ar (a) or air (b) atmosphere. □: acetaldehyde, □: acetaldehyde diethyl acetal (acetal), ■: acetic acid.

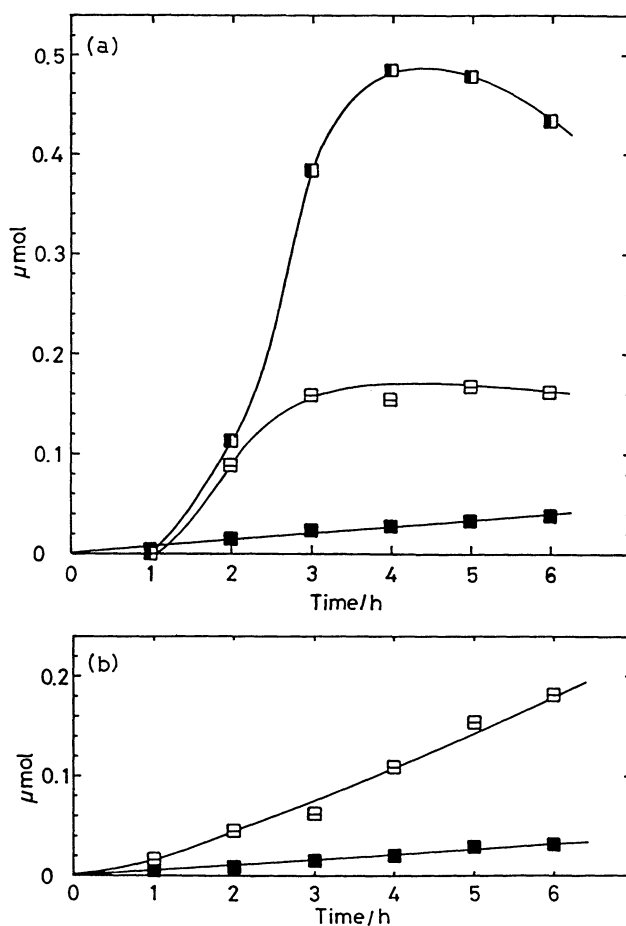
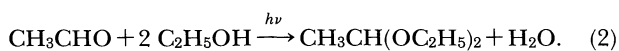


Fig. 2. Evolution of gaseous products from 2.0 ml ethanol vs. illumination time for a blank test without any TiO<sub>2</sub> under Ar (a) or air (b) atmosphere. ■: CH<sub>4</sub>, □: CO<sub>2</sub>, ■: H<sub>2</sub>.

nation times less than 1 h, and therefore appear to be formed in the following way:

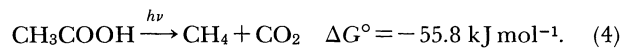


Actually, this reaction was confirmed by the formation of acetal and H<sub>2</sub>O from a mixture of CH<sub>3</sub>CHO (0.2 ml) and C<sub>2</sub>H<sub>5</sub>OH (1.8 ml) under an Ar atmosphere without TiO<sub>2</sub>. Acetic acid is formed as proposed by Sakata and Kawai,<sup>1)</sup>



The formation of CH<sub>3</sub>COOH and H<sub>2</sub> was also observed in a mixture of CH<sub>3</sub>CHO (0.2 ml) and H<sub>2</sub>O (1.8 ml) under Ar. In addition, CH<sub>4</sub> and CO<sub>2</sub> from Eq. 4, shown later, were evolved. The H<sub>2</sub>O in Eq. 3 is contained as a small amount of impurity in ethanol and is provided by Eq. 2 as well as by the oxidation of C<sub>2</sub>H<sub>5</sub>OH by O<sub>2</sub> under an air atmosphere.<sup>8)</sup> Actually, H<sub>2</sub>O formation under air was more than that under an Ar atmosphere.

No evolution of CH<sub>4</sub> and CO<sub>2</sub> was detected for illumination times less than 1 h under Ar. This is because the decomposition of CH<sub>3</sub>COOH gives an evolution of CH<sub>4</sub> and CO<sub>2</sub>, as reported by Kraeutler and Bard,<sup>13)</sup> and no CH<sub>3</sub>COOH was formed during the initial stage.



By the way, in spite of the formation of CH<sub>3</sub>COOH and CO<sub>2</sub> under air, no CH<sub>4</sub> was detected. One possible reason for no CH<sub>4</sub> evolution involves the oxidation of CH<sub>4</sub> by O<sub>2</sub> in air.

Figure 3 shows the formation of CH<sub>3</sub>CHO from ethanol versus the illumination time observed for four TiO<sub>2</sub> catalysts under an atmosphere of Ar and that of air. Because of the higher yield with each TiO<sub>2</sub>, compared to the yield of the blank test, all of the TiO<sub>2</sub> contributes to the formation of CH<sub>3</sub>CHO. Acetaldehyde is also formed by the reduction of TiO<sub>2</sub>, itself, as shown in Eq. 5 for the following reason. Buss and co-workers proposed the formation of Ti<sub>2</sub>O<sub>3</sub> through a color change of the illuminated TiO<sub>2</sub> in normal

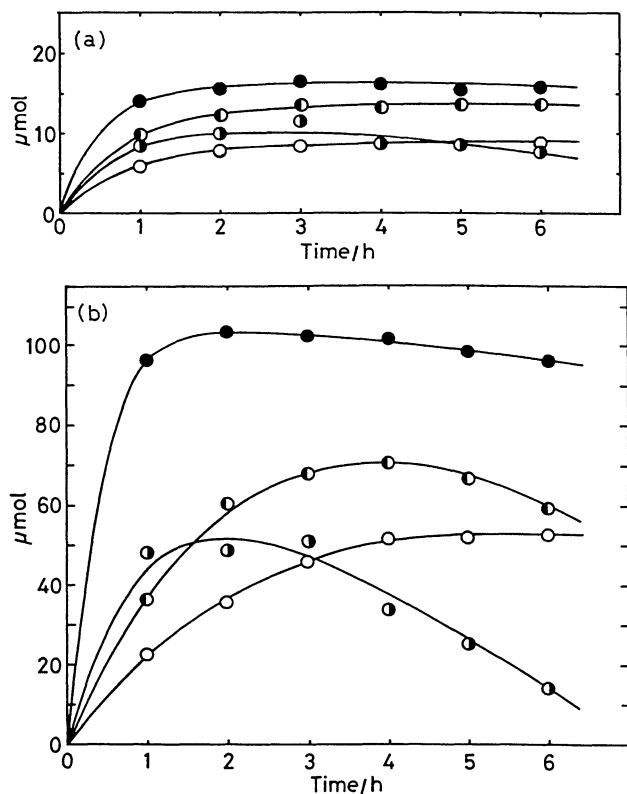
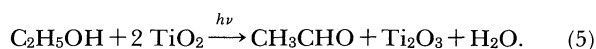


Fig. 3. Formation of acetaldehyde vs. illumination time for suspensions of 30 mg  $\text{TiO}_2$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. ○: anatase (Aldrich), ●: rutile (Aldrich), ●: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

primary alcohols.<sup>14)</sup> Nishimotol et al. demonstrated the cause for the color change by which  $\text{Ti}_2\text{O}_3$  is formed by a reduction of  $\text{TiO}_2$  with 2-propanol.<sup>9)</sup> Judging from these two reports, the color change of illuminated  $\text{TiO}_2$  in the present work is considered to be caused by a partial formation of  $\text{Ti}_2\text{O}_3$  due to the reduction of  $\text{TiO}_2$  with ethanol,



The molar quantities of  $\text{TiO}_2$  required to react with 2.0 ml ( $343 \times 10^2 \mu\text{mol}$ ) of ethanol are  $686 \times 10^2 \mu\text{mol}$ , as can be seen from Eq. 5. However, 30 mg ( $375 \mu\text{mol}$ ) of  $\text{TiO}_2$  is about 1/200 of the value of  $\mu\text{mol}$  required to react with 2.0 ml of ethanol. Therefore, the  $\text{TiO}_2$  may be further reduced with a large excess of the ethanol,



If only gaseous  $\text{O}_2$  in the reaction tube contributed to the formation for  $\text{CH}_3\text{CHO}$ , the ratio of  $\text{CH}_3\text{CHO}$  formation under Ar to that under air in a blank test should be the same as that with  $\text{TiO}_2$ . However, the formation of  $\text{CH}_3\text{CHO}$  with most  $\text{TiO}_2$  catalysts under air is above about 5-times that under Ar, while its formation in a blank test under air is approxi-

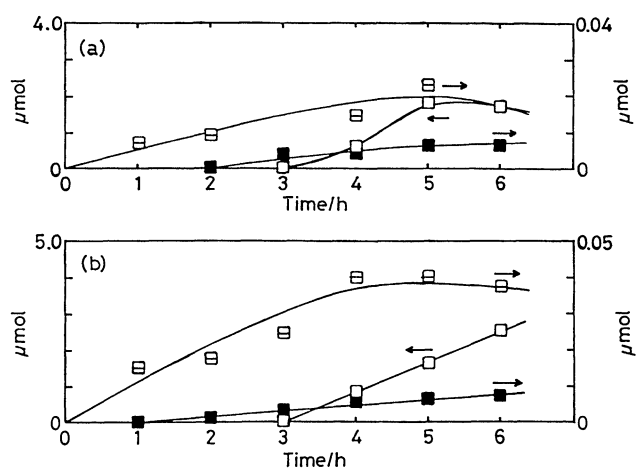


Fig. 4. Formation of products vs. illumination time for suspension of 30 mg  $\text{Ti}_2\text{O}_3$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. □: acetaldehyde, ◻:  $\text{CO}_2$ , ■:  $\text{H}_2$ .

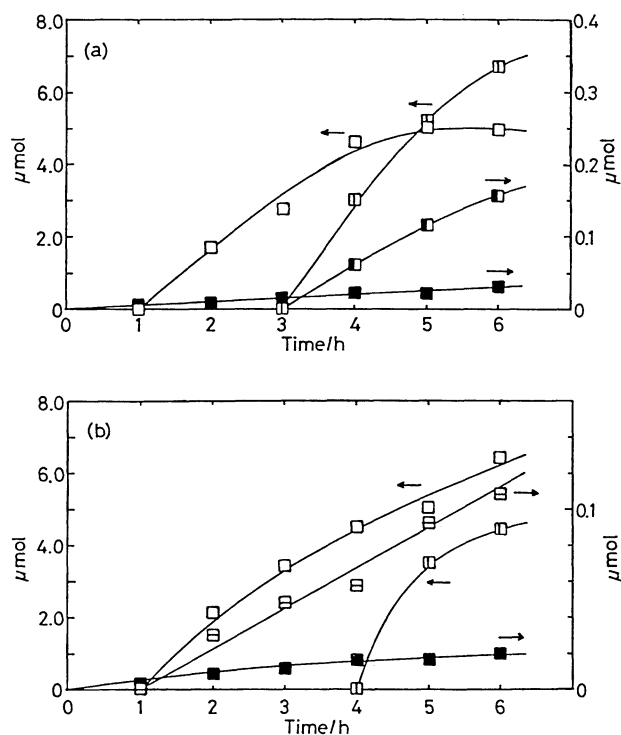


Fig. 5. Formation of products vs. illumination time for suspension of 30 mg  $\text{TiO}$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. □: acetaldehyde, ◻: acetal, ■:  $\text{CH}_4$ , ◻:  $\text{CO}_2$ , ■:  $\text{H}_2$ .

mately twice that under Ar. Such a difference between the ratio with the  $\text{TiO}_2$  and that in the blank test is remarkably observed for other products, as shown later, since the yields of the other products under Ar in the blank test are roughly the same as those under air, in contrast to the larger difference in the yields with the  $\text{TiO}_2$  than the result for  $\text{CH}_3\text{CHO}$ . Consequently, the active  $\text{O}_2$  from the reoxidized

$\text{TiO}_2$ ) by  $\text{O}_2$  in air seems to be the reason for the higher yield of  $\text{CH}_3\text{CHO}$  under air than that under Ar. If this assumption were correct, the color change<sup>9,14</sup> due to the reduction of  $\text{TiO}_2$  observed under air should be much less than that under Ar; further,  $\text{O}_2$  in the reaction tube must be decreased, and water must be formed. In fact, these three observations were obtained. To make sure of this estimate, we tried to produce  $\text{CH}_3\text{CHO}$  with  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}$  corresponding to the reduction product of  $\text{TiO}_2$ ; these two catalysts gave much fewer products, as shown in Figs. 4 and 5, respectively. Accordingly, the retarding photochemical reduction of  $\text{TiO}_2$  under an air atmosphere led to much  $\text{CH}_3\text{CHO}$  formation.

Figure 6 shows the formation of acetal. Under Ar, in spite of the higher yield of  $\text{CH}_3\text{CHO}$  with P-25 and rutile (Furuuchi), compared to the rutile (Aldrich), these two  $\text{TiO}_2$  gave no acetal. Although there was no large difference between the yield of  $\text{CH}_3\text{CHO}$  with rutile (Aldrich) and that with anatase, the anatase yielded no acetal. It is therefore evident that these three  $\text{TiO}_2$  of P-25, rutile (Furuuchi), and anatase did not catalyze the formation of acetal under Ar.

In the case of an air atmosphere, all of the  $\text{TiO}_2$ , except for anatase, gave more acetal than that under Ar. That only anatase gave no acetal is interesting, since this  $\text{TiO}_2$  produces  $\text{CH}_3\text{CHO}$ .

Figure 7 shows the formation of  $\text{CH}_3\text{COOH}$ . The water in Eq. 3 required to produce  $\text{CH}_3\text{COOH}$  is further supplied from Eqs. 5 and 6, and the evolution of  $\text{C}_2\text{H}_4$  from  $\text{C}_2\text{H}_5\text{OH}$ ,<sup>8,10</sup> besides being available from only a small amount of  $\text{H}_2\text{O}$  in ethanol and  $\text{H}_2\text{O}$

from Eq. 2.

In spite of no large difference in the yield of  $\text{CH}_3\text{CHO}$  (Fig. 3, under Ar), no  $\text{CH}_3\text{COOH}$  can be detected on both rutiles (Aldrich and Furuuchi) and P-25 in Ar. However, it seems reasonable to assume that these three  $\text{TiO}_2$  may also produce in practice  $\text{CH}_3\text{COOH}$ , due to  $\text{CH}_4$  and  $\text{CO}_2$  formation in Eq. 4 from the  $\text{CH}_3\text{COOH}$  formed with all of the  $\text{TiO}_2$  tested (as is shown later). Each yield of their  $\text{CH}_3\text{COOH}$ , however, seems to be much less than the yield with anatase, and such a minor  $\text{CH}_3\text{COOH}$  is almost consumed during the evolution of  $\text{CH}_4$  and  $\text{CO}_2$ , accordingly to Eq. 4. If a slight amount of  $\text{CH}_3\text{COOH}$  exists in the reaction solution after decomposition to  $\text{CH}_4$  and  $\text{CO}_2$ , it is almost adsorbed on the surface of the analysis path of the gas chromatograph because of the high adsorptive property of the acid. The more rapid decomposition rate of  $\text{CH}_3\text{COOH}$  with both rutiles and P-25 than anatase may have also been a cause for no detection of the acid.

All of the  $\text{TiO}_2$  in an air atmosphere catalyzes the formation of  $\text{CH}_3\text{COOH}$  and gives much more  $\text{CH}_3\text{COOH}$  than that under Ar. Anatase did not give as much  $\text{CH}_3\text{CHO}$  as that shown in Fig. 3, but never-

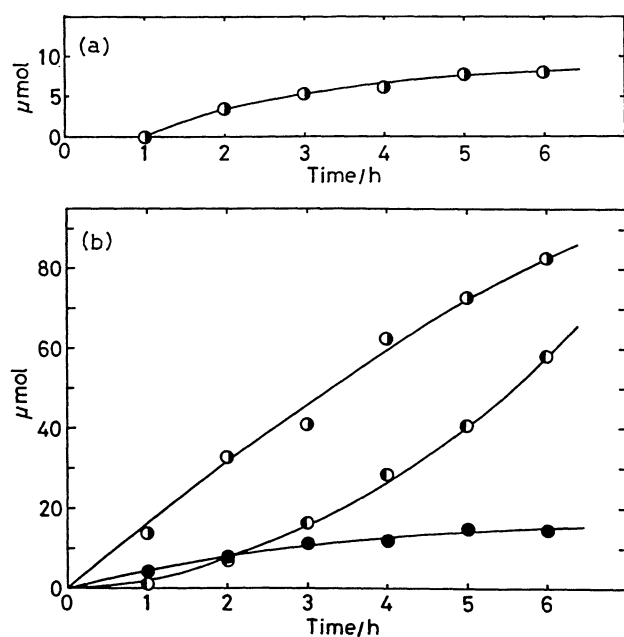


Fig. 6. Formation of acetal vs. illumination time for suspensions of 30 mg  $\text{TiO}_2$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. ●: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

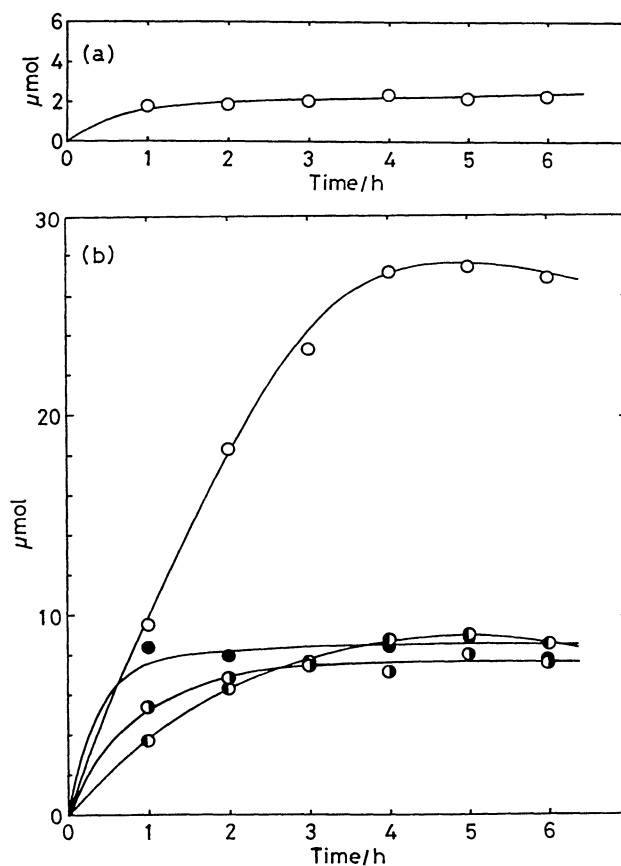


Fig. 7. Formation of acetic acid vs. illumination time for suspensions of 30 mg  $\text{TiO}_2$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. ○: anatase (Aldrich), ◐: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

theless showed a much higher  $\text{CH}_3\text{COOH}$  yield than did the other  $\text{TiO}_2$  catalysts. This is because only anatase did not give acetal (Fig. 6), which is produced from  $\text{CH}_3\text{CHO}$ , as shown in Eq. 2. That is to say, because  $\text{CH}_3\text{CHO}$  with anatase produced  $\text{CH}_3\text{COOH}$  without being used up in the formation of acetal, the anatase could give the greatest  $\text{CH}_3\text{COOH}$  yield.

Figure 8 shows the evolution of  $\text{CH}_4$ . In the case of an Ar atmosphere, since no evolution of  $\text{CH}_4$  took place in the blank test during the initial time, all of the  $\text{TiO}_2$  catalyzed evolving  $\text{CH}_4$  at that time. However, since the yield of  $\text{CH}_4$  was much less than that in the blank test, oxidation of the  $\text{CH}_4$  by the  $\text{O}_2$  released from  $\text{TiO}_2$  seems to be the reason for this result.

All of the  $\text{TiO}_2$  under an air atmosphere catalyzed the evolution of  $\text{CH}_4$ , since no  $\text{CH}_4$  evolved in a blank

test under air. The result that  $\text{CH}_4$  evolution under air is more than that under Ar is consistent with a similar data observed regarding  $\text{CH}_3\text{COOH}$  formation, since  $\text{CH}_4$  evolves from  $\text{CH}_3\text{COOH}$ .

Figure 9 shows the evolution of  $\text{CO}_2$ . All of the  $\text{TiO}_2$  gives much more  $\text{CO}_2$  under air than that under an Ar atmosphere, because  $\text{CH}_3\text{COOH}$  formation under air is much higher than that under Ar.

Because the evolution of  $\text{H}_2$  and  $\text{C}_2\text{H}_2$  under Ar and air had been previously reported,<sup>8,10</sup> it was omitted.

As described above, air has been found to be effective for the formation of all products; to prove such an effect, further experiments were performed under an  $\text{O}_2$  atmosphere.

Figure 10 shows the formation of products from ethanol observed for a blank test under an  $\text{O}_2$  atmosphere. Although trace amounts of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_4$  were detected, no  $\text{C}_2\text{H}_4$  evolved. Only the yield of  $\text{CO}_2$  was more than that under air (Fig. 2).

Figure 11 shows the formation of liquid products from ethanol versus the illumination time observed for the  $\text{TiO}_2$  (rutile, Furuuchi) under an atmosphere of  $\text{O}_2$ . All of the products were formed in greater quantities than those under air.

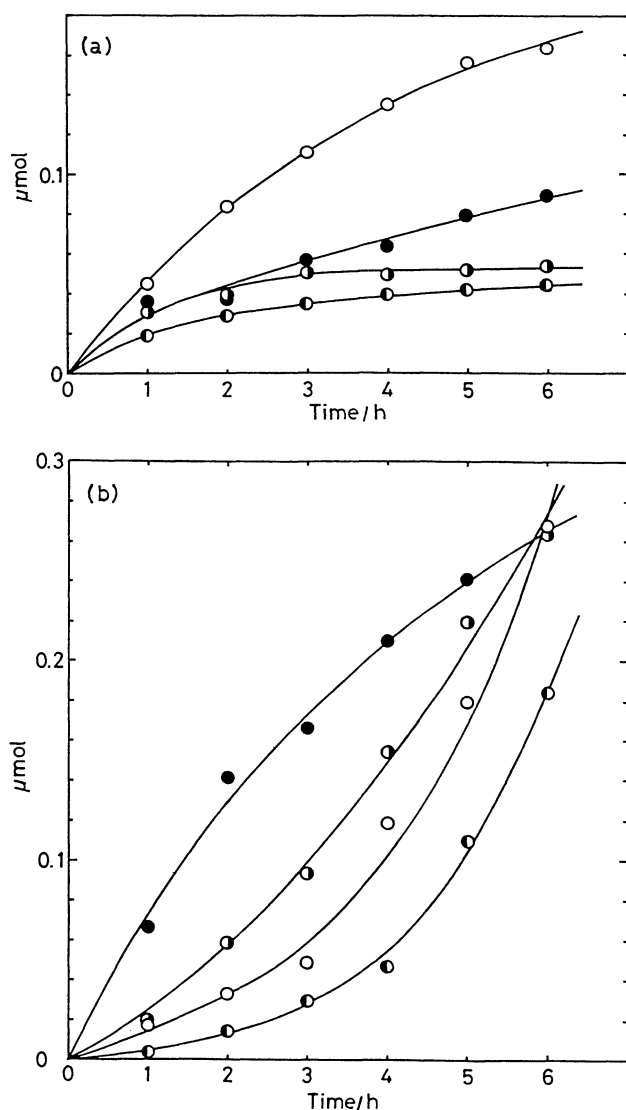


Fig. 8. Evolution of  $\text{CH}_4$  vs. illumination time for suspensions of 30 mg  $\text{TiO}_2$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. ○: anatase (Aldrich), ●: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

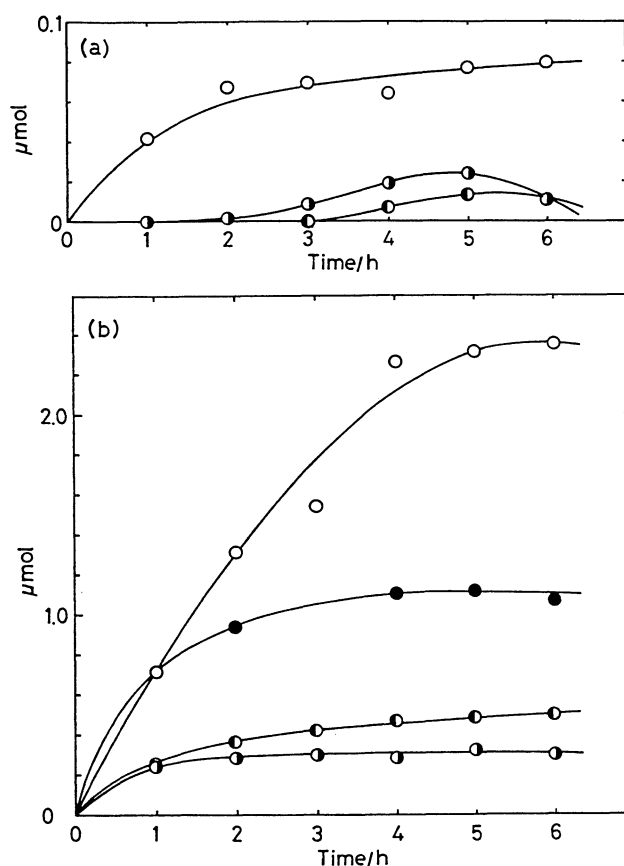


Fig. 9. Evolution of  $\text{CO}_2$  vs. illumination time for suspensions of 30 mg  $\text{TiO}_2$  in 2.0 ml ethanol under Ar (a) or air (b) atmosphere. ○: anatase (Aldrich), ●: rutile (Aldrich), ◐: rutile (Furuuchi), ●: P-25 (Nippon Aerosil).

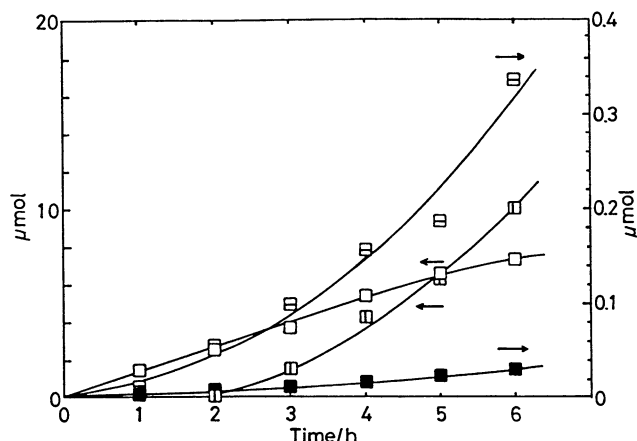


Fig. 10. Formation of products from 2.0 ml ethanol vs. illumination time for a blank test without any  $\text{TiO}_2$  under  $\text{O}_2$  atmosphere.  $\square$ : acetaldehyde,  $\square$ : acetaldehyde diethyl acetal (acetal),  $\square$ :  $\text{CO}_2$ ,  $\blacksquare$ :  $\text{H}_2$ .

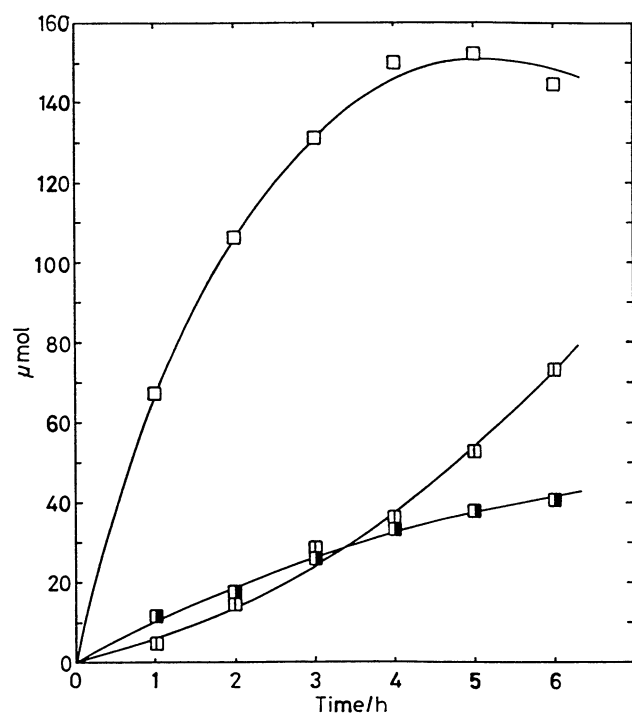


Fig. 11. Formation of liquid products vs. illumination time for suspension of 30 mg  $\text{TiO}_2$  (rutile, Furuuchi) in 2.0 ml ethanol under  $\text{O}_2$ .  $\square$ : acetaldehyde,  $\square$ : acetaldehyde diethyl acetal (acetal),  $\blacksquare$ : acetic acid.

Figure 12 shows the formation of gaseous products with  $\text{TiO}_2$  (rutile, Furuuchi) under  $\text{O}_2$ . All of the gaseous products, except for  $\text{CH}_4$ , were formed in greater quantities than those under an air atmosphere. One possible reason why only  $\text{CH}_4$  evolution is less than that under air is as given below. In a blank test, no  $\text{CH}_4$  was formed under  $\text{O}_2$  and air, although it was evolved under Ar. Judging from

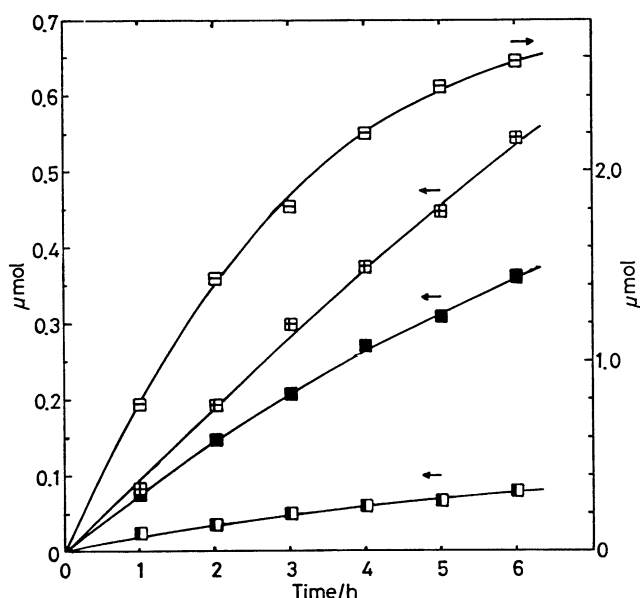


Fig. 12. Evolution of gaseous products vs. illumination time for suspension of 30 mg  $\text{TiO}_2$  (rutile, Furuuchi) in 2.0 ml ethanol under  $\text{O}_2$ .  $\square$ :  $\text{C}_2\text{H}_4$ ,  $\square$ :  $\text{CH}_4$ ,  $\square$ :  $\text{CO}_2$ ,  $\blacksquare$ :  $\text{H}_2$ .

these results, even if  $\text{CH}_4$  evolved more than that under air, it was further oxidized by excess  $\text{O}_2$  in the reaction tube. The fact that the  $\text{CO}_2$  yield was about 5-times that under air supports this assumption.

The yield of  $\text{C}_2\text{H}_4$  vs. the illumination time is approximately linear, while under air it gave a downward curvature.<sup>8)</sup> The reason for such a high activity of  $\text{TiO}_2$  is a smaller reduction of part of the  $\text{TiO}_2$  than that under air. Actually, no color change<sup>9,14)</sup> due to a reduction of  $\text{TiO}_2$  was observed, in contrast to the result under air.

The differences among the yields regarding products with  $\text{TiO}_2$  under Ar, air, and  $\text{O}_2$  was much larger than that in blank tests under these three atmospheres; the yields with  $\text{TiO}_2$  increased in the order  $\text{Ar} < \text{air} < \text{O}_2$  atmosphere. Consequently, it has become apparent that active  $\text{O}_2$  from reoxidized  $\text{TiO}_2$  by  $\text{O}_2$  in the reaction tube has a considerably greater effect on the photolysis of ethanol with  $\text{TiO}_2$  than does gaseous  $\text{O}_2$  present in the reaction tube.

## References

- 1) T. Sakata and T. Kawai, *Chem. Phys. Lett.*, **80**, 341 (1981).
- 2) P. Pichat, J.-M. Herrmann, J. Disdier, H. Courbon, and M.-N. Mozzanega, *Nouv. J. Chim.*, **5**, 627 (1981).
- 3) E. Borgarello and E. Pelizzetti, *Chim. Ind. (Milan)*, **65**, 474 (1983).
- 4) M. Kawai, T. Kawai, S. Naito, and K. Tamaru, *Chem. Phys. Lett.*, **110**, 58 (1984).
- 5) S. Nishimoto, B. Ohtani, and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, **81**, 2467 (1985).
- 6) A. Hamano and S. Matsuo, *Kenkyu Hokoku-Sasebo*

*Kogyo Koto Senmon Gakko*, **23**, 49 (1986).

7) G. F. Huttig, *Kolloid Z.*, **106**, 166 (1944); S. Kato and F. Masuo, *Kogyo Kagaku Zasshi*, **67**, 1136 (1964).

8) K. Iseda, *Chem. Express*, **5**, 729 (1990).

9) S. Nishimoto, B. Ohtani, A. Sakamoto, and T. Kagiya, *Nippon Kagaku Kaishi*, **2**, 246 (1984).

10) K. Iseda, *Chem. Express*, **5**, 209 (1990).

11) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka, and

S. Nagakura, *Bull. Chem. Soc. Jpn.*, **37**, 417 (1964).

12) S. Patai, "The Chemistry of the Carbonyl Group," Interscience Publishers, London (1966), p. 828.

13) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 2239 (1978).

14) A. D. Buss, M. A. Malati, and R. Atkinson, *J. Oil Col. Chem. Assoc.*, **59**, 369 (1976).

---