Photocatalytic Degradation and Dimerization of t-Butyl Alcohol by Aqueous Suspension of Platinized Titanium Dioxide

Sei-ichi Nishimoto, Bunsho Ohtani, Hiroshi Shirai, and Tsutomu Kagiya *
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Photoirradiation ($\lambda_{ex} > 300$ nm) of argon-purged aqueous suspension of platinized TiO_2 containing t-butyl alcohol at 27 ± 3 °C led to the formation of hydrogen, methane, and ethane in the gas phase, and acetone, t-pentyl alcohol (Pn^{t}OH), and 2,5-dimethylhexane-2,5-diol (2,5-DH) in the solution phase. While TiO_2 without Pt showed little activity, the product yields increased linearly upon increasing the amount of Pt loading up to 10 wt%. The increasing concentrations of Bu^{t}OH up to 0.2M enhanced the product yields, owing to the increase in the amount of adsorbed Bu^{t}OH on the TiO_2 surface. The acetone formation predominated in the presence of either oxygen or silver salt. Product distributions obtained by the γ-irradiation under N_2O-saturated conditions and by treatment with Fenton's reagent were similar to that of the photocatalytic reaction by platinized TiO_2.

Among semiconductor materials titanium dioxide (TiO_2) has been an important photocatalyst for both oxidation and reduction of organic or inorganic substrates, which are caused by holes and electrons formed upon near-u.v.-irradiation.[1–3] Modification of the TiO_2 surface by partial coverage with platinum is effective for the reduction of protons to H_2 by photoexcited electrons.[4] Primary and secondary alcohols such as methanol,[5] ethanol,[6] propan-2-ol,[7–10] and poly(vinyl alcohol)[11,12] undergo photocatalytic dehydrogenation by platinized TiO_2 suspended in the aqueous solution. However, the photocatalytic reaction of tertiary alcohols remains the subject of further characterization.

Arimitsu and his co-workers reported[13] the photocatalytic formation of a dimeric product, 2,5-dimethylhexane-2,5-diol (2,5-DH), together with H_2 from t-butyl alcohol in a deaerated aqueous suspension of platinized TiO_2. This paper reports a detailed study on the photocatalytic reaction of Bu^{t}OH under deaerated and aerated conditions. The photocatalytic reaction mechanism is discussed by comparing the product distribution with those of oxidation processes induced by γ-radiolysis and Fenton's reagent.

Experimental

Materials.—Titanium dioxide powder [>99% anatase, TiO_2(A)] was obtained from Merck and used without further activation. Rutile TiO_2 powder [TiO_2(R)] was prepared by calcination of TiO_2(A) at 1 200 °C for 10 h in an electric furnace. This treatment transformed anatase almost quantitatively into rutile, as determined by *X*-ray diffraction analysis.[14] Platinized TiO_2 catalyst was prepared by powdering a mixture of anatase or rutile with 5 wt% platinum black (Nakarai Chemicals).[9,10] Palladium and ruthenium dioxide loadings were performed in a similar way. Water was passed through an ion exchange resin and distilled immediately before use. The other chemicals including Bu^{t}OH were of analytical grade and used as received.

Apparatus.—A 400 W high-pressure mercury arc (Eiko-sha 400) set to a merry-go-round apparatus was used as the light source. Gaseous products liberated during irradiation ($\lambda_{ex} >$ 300 nm) were measured by g.c., using a Shimadzu GC 4A [for H_2 and O_2, equipped with a thermal conductivity detector, column 60—80 mesh molecular sieve 5A (3 mmφ × 3 m), Ar carrier at 130 °C] and a GC 6A [for CH_4 and C_2H_6, equipped with an f.i.d., column 50—80 mesh Porapak R (3 mmφ × 2 m), N_2 carrier at 90 °C]. The distribution of deuterium-labelled products (D_2, HD, and CH_3D) obtained from the photoirradiated D_2O solution was determined by mass spectrometry on an Ulvac MSQ 400 instrument. Non-volatile products in the reaction mixture were analysed by a Shimadzu GC 6A [for acetone, Bu^{t}OH, and t-pentyl alcohol (Pn^{t}OH), equipped with an f.i.d., column 20% poly(ethylene glycol) 20 M on 60—80 mesh Celite 545 (3 mmφ × 2 m), N_2 carrier at 90 °C] and GC 7A [for 2,5-DH, equipped with an f.i.d., column 60—80 mesh Tenax GC (3 mmφ × 1 m), N_2 carrier at 200 °C]. Atomic absorption spectrometry of Ag^+ ions was carried out on a Jarrel–Ash AA 8200 spectrometer.

Procedure.—The powdered catalyst (TiO_2–Pt, typically 50 mg) and solvent [distilled water, aqueous NaOH (1M) solution, or aqueous Ag_2SO_4 (0.025M) solution; 5.0 cm^3] was placed in a glass tube (18 mmφ × 180 mm, transparent for exciting-light wavelengths >300 nm), purged for 30 min with Ar, and then sealed off with a rubber stopper. An aerated suspension was prepared in the similar way using an O_2 stream. The substrate Bu^{t}OH was injected, just before irradiation, through the stopper by microsyringe. The suspension thus prepared was irradiated under magnetic stirring at 27 ± 3 °C.

After irradiation, a portion of the gaseous products was collected by syringe and analysed. The suspension was centrifuged to separate the catalyst and then the aqueous solution was subjected to g.c. analysis. In experiments using silver salt, the separated TiO_2 powder was washed repeatedly with distilled water, dried overnight at 70 °C, and treated with HNO_3 (*ca.* 13M) to dissolve photodeposited silver metal. The resulting suspension of bleached TiO_2 was diluted with distilled water and centrifuged to measure Ag^+ concentration.

γ-Irradiation of aqueous Bu^{t}OH solution under N_2O was carried out in the sealed glass tubes at room temperature with a ^{60}Co γ-ray source at a dose rate of 380 Gy h^{-1}. Oxidation of Bu^{t}OH with Fenton's reagent was performed using aqueous solutions (5.0 ml) of $FeSO_4$ and H_2O_2 (180 μmol).

Results and Discussion

Photocatalytic Reaction of Bu^{t}OH *by Aqueous Suspension of Platinized* TiO_2.—Photoirradiation ($\lambda_{ex} > 300$ nm) of the argon-purged aqueous suspension of platinized TiO_2 (TiO_2–

Table. Product distribution in the photocatalysis of t-butyl alcohol by aqueous suspension of TiO_2–Pt

Run	Catalyst[a]	Conditions[b]		Yield (μmol)					
				H_2	CH_4	C_2H_6	acetone	Pn'OH	2,5-DH
1	T	NaOH	Ar[c]	0.1	0.4	≃0	0.6	≃0	0.2
2	T–Pt	H_2O	Ar[d]	2.5	0.2	≃0	1.0	0.2	6.1
3	T–Pt	NaOH	Ar[d]	35.3	12.1	1.3	15.1	7.4	15.9
4	T–Pt	H_2SO_4	Ar[d]	1.3	0.2	≃0	1.3	≃0	0.8
5	T–Pt	H_2O	O_2[d]	≃0	0.3	≃0	28.2	0.2	5.8
6	T–Pt	NaOH	O_2[d]	17.6	6.8	0.7	28.8	5.3	9.9
7	T–Pt	H_2SO_4	O_2[d]	≃0	0.9	≃0	39.6	≃0	1.4
8	T–Pd	H_2O	Ar[c]	3.6	0.4	≃0	1.3	0.3	7.5
9	T–Pd	NaOH	Ar[c]	16.4	10.1	0.6	14.3	5.4	14.5
10	T–RO	H_2O	Ar[c]	0.2	≃0	≃0	0.2	≃0	0.3
11	T–RO	NaOH	Ar[c]	1.2	0.6	≃0	1.1	0.2	0.9
12[g]	T–Pt	Ag_2SO_4	Ar[c]	≃0	1.5	2.1	41.3	0.1	≃0
13[g]	T	Ag_2SO_4	Ar[c]	≃0	1.5	3.0	35.5	0.1	≃0
14[g]	T(R)	Ag_2SO_4	Ar[c]	≃0	≃0	≃0	9.1	≃0	≃0
15[h]		H_2O	N_2O[e]	1.7	0.2	≃0	2.2	0.4	4.9
16[h]		NaOH	N_2O[e]	1.9	0.7	0.2	4.4	2.0	3.8
17		$FeSO_4$	Ar[f]	≃0			4.1	≃0	19.8

[a] T = anatase TiO_2 (Merck), T–Pt = anatase TiO_2 with 5 wt% of platinum black, T–Pd = anatase TiO_2 with 5 wt% of palladium black, T–RO = anatase TiO_2 with 10 wt% ruthenium dioxide, and T(R) = rutile TiO_2. [b] NaOH: 1M-NaOH, H_2O: distilled water, H_2SO_4: 0.5M-H_2SO_4, Ag_2SO_4: 0.025M-Ag_2SO_4, and $FeSO_4$: 0.04M solution. [c] Irradiation ($\lambda_{ex} > 300$ nm) for 10 h. [d] Irradiation for 5 h. [e] γ-Irradiation (^{60}Co, 72.8 kGy). [f] Fenton's reagent containing 180 μmol of H_2O_2. [g] Ag metal deposition was also observed; run 12: 212.5, run 13: 169.8, and run 14: 121.2 μmol. [h] N_2 was also determined; run 15; 13.7, and run 16: 15.8 μmol.

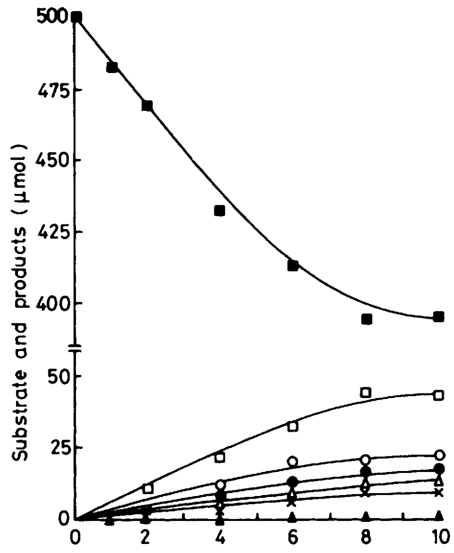

Figure 1. Time course of the photocatalytic reaction of 0.5 mmol-Bu'OH in 5 ml of 1M-NaOH solution with 50 mg of TiO_2–Pt under Ar: ■, Bu'OH; □, H_2; ○, 2,5-DH; ●, acetone; △, CH_4; X, Pn'OH; and ▲, C_2H_6

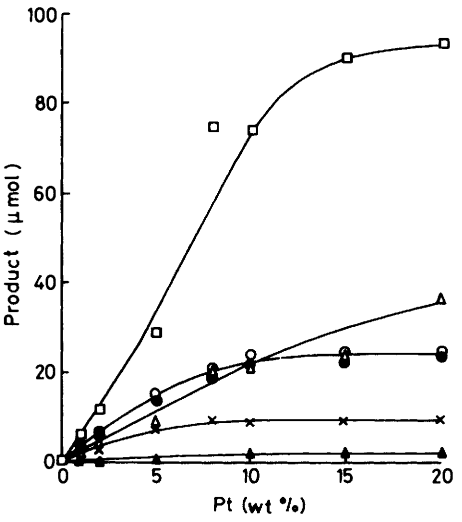

Figure 2. Effects of Pt loading on the yields of products: symbols are as in Figure 1

Pt) containing Bu'OH produced H_2, CH_4, and C_2H_6 in the gas phase of the reaction mixture. Simultaneously, formation of 2,5-DH, acetone, and Pn'OH was observed in the solution phase (Table). These products were not produced in the dark, nor with irradiation in the absence of TiO_2–Pt. It is evident that greater product yields can be obtained under alkaline conditions. Furthermore, the formation of acetone as an oxidation product predominated over the other products in the presence of O_2 or Ag_2SO_4.

Figure 1 shows the representative time course of the photocatalytic reaction of Bu'OH by TiO_2–Pt in alkaline solution under argon. The starting material Bu'OH decreased and the products increased linearly with irradiation time up to 6 h. Further irradiation was less effective for the photocatalytic reaction. A possible reason for such deactivation of the TiO_2–Pt catalyst is detachment of Pt particles from the TiO_2 surface during photoirradiation, as noted from the increased formation of Pt aggregate. This result shows the importance of contact between Pt particles and the TiO_2 surface in obtaining efficient photocatalytic activity.

Photoirradiation of a 1M-NaOH solution (5 ml) of 0.1M-Bu'OH was also carried out under Ar for 5 h with varying amounts of Pt loading onto TiO_2 (50 mg). Similar products as listed in the Table were obtained by use of TiO_2 without Pt loading, but the yields were negligibly small. The product yields in both gas and solution phases (Figure 2) increased linearly upon increasing Pt up to 10 wt%. Excess of Pt over 10 wt% led to little increase in the apparent activity of TiO_2. Loading of Pd and RuO_2, instead of Pt, onto TiO_2 also enhanced the photocatalytic reaction, the effect of which was smaller than that of Pt loading (see Table).

Stoicheiometry of the TiO_2–Pt-*Catalysed Photoreaction of* Bu^{t}OH.—The net reactions which account for the observed products are (1)—(4). In accord with reactions (1)—(4), the

$$(CH_3)_3COH \longrightarrow (CH_3)_2CO + CH_4 \quad (1)$$

$$2(CH_3)_3COH \longrightarrow 2(CH_3)_2CO + CH_3CH_3 + H_2 \quad (2)$$

$$2(CH_3)_3COH \longrightarrow (CH_3)_2CO + CH_3CH_2C(CH_3)_2OH + H_2 \quad (3)$$

$$2(CH_3)_3COH \longrightarrow (CH_3)_2C(OH)CH_2CH_2C(CH_3)_2OH + H_2 \quad (4)$$

number of moles of $CH_4 + 2 \times H_2$ as gaseous products was approximately equal to that of converted Bu^{t}OH; the linear relationship shown in Figure 3 gave a proportionality constant of near unity (0.90). Acetone + Pn^{t}OH + 2 × 2,5-DH should be equal to converted Bu^{t}OH, and we observed *ca.* 70% recovery of Bu^{t}OH as the form of these products (Figure 3). Furthermore, reactions (1)—(3) predict that the photocatalytic conversion of Bu^{t}OH into acetone accompanies the formation of CH_4, C_2H_6, and Pn^{t}OH. Support for this prediction comes from the observation that the number of moles of $CH_4 + 2 \times C_2H_6$ + Pn^{t}OH is close to that of acetone (Figure 4).

Mechanism of the TiO_2–Pt-*Catalysed Photoreaction of* Bu^{t}OH.—The observed reaction characteristics are rationalized by the following mechanism. In the initial step, the dispersed TiO_2 particle absorbs exciting light to generate a hole-electron pair [reaction (5)]. Pt loaded on TiO_2 catalyses reduction of protons to H_2 by the photogenerated electrons (e) [reaction (6)], which can promote charge separation of the h^+—e pair and thereby increase the overall activity of TiO_2 photocatalyst (see Figure 2).

$$TiO_2 + h\nu \longrightarrow h^+ + e \quad (5)$$

$$H^+ + e + Pt \longrightarrow Pt\text{–}H \rightleftharpoons \tfrac{1}{2} H_2 + Pt \quad (6)$$

Based on photoirradiation in D_2O (99%) which produced D_2 (91.6% selectivity) with small amounts of HD (8.0%) and H_2 (0.4%), the direct source of H_2 is presumably H_2O but not Bu^{t}OH.

The conversion of Bu^{t}OH to carbon-containing products occurs as a result of hole (h^+) reaction. There are two possible modes of the h^+ reaction leading to decomposition of Bu^{t}OH, *i.e.* direct one-electron oxidation of Bu^{t}OH adsorbed on the TiO_2 [reaction (7)] and oxidation of the surface hydroxy group of TiO_2 followed by hydrogen abstraction of the intermediate hydroxyl radical from Bu^{t}OH [reactions (8) and (9)]. Clearly, the products Pn^{t}OH and 2,5-DH favour the intermediacy of 2-methyl-2-hydroxypropyl radical rather than t-butylalkoxyl radical. The alkyl radical can also be a common intermediate for acetone formation *via* β-scission, although the possibility of an alkoxyl radical intermediate was not ruled out.

$$(CH_3)_3COH_{ads} + h^+ \longrightarrow [(CH_3)_3COH]^{+\cdot}_{ads} \longrightarrow (CH_3)_3C\text{–}O\cdot_{ads} + H^+ \quad (7)$$

$$-\overset{|}{\underset{|}{Ti}}\text{–}OH + h^+ \longrightarrow -\overset{|}{\underset{|}{Ti}}{}^+\cdot OH\ (\equiv \cdot OH_{ads}) \quad (8)$$

$$(CH_3)_3COH_{ads} + {}^{\cdot}OH_{ads} \longrightarrow {}^{\cdot}CH_2C(CH_3)_2OH_{ads} + H_2O \quad (9)$$

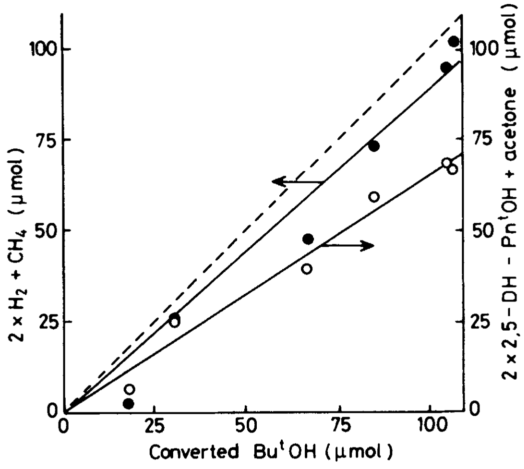

Figure 3. Relationships between the amount of products and that of converted Bu^{t}OH in the photocatalytic reaction in 1M-NaOH solution under Ar: ●, $2 \times H_2 + CH_4$ *versus* converted Bu^{t}OH; ○, 2 × 2,5-DH + Pn^{t}OH + acetone *versus* converted Bu^{t}OH

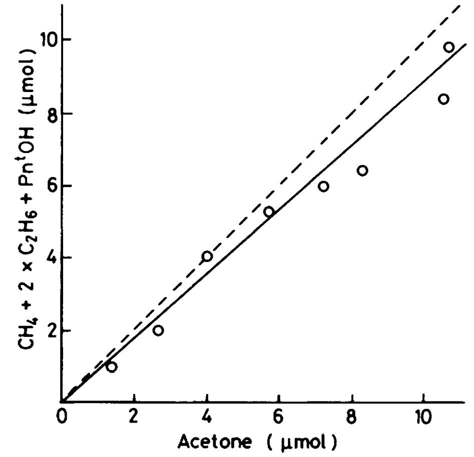

Figure 4. Relationship between the amount of $CH_4 + 2 \times C_2H_6$ + Pn^{t}OH and that of acetone as products in the photocatalytic reaction of Bu^{t}OH in 1M-NaOH solution under Ar

Thus, the secondary reaction processes (10)—(14) may be

$${}^{\cdot}CH_2C(CH_3)_2OH \xrightarrow{\beta\text{-scission}} [CH_2{=}C(CH_3)OH + {}^{\cdot}CH_3] \rightleftharpoons (CH_3)_2CO + {}^{\cdot}CH_3 \quad (10)$$

$${}^{\cdot}CH_3 + Pt\text{–}H \longrightarrow CH_4 + Pt \quad (11)$$

$$2\,{}^{\cdot}CH_3 \longrightarrow CH_3CH_3 \quad (12)$$

$${}^{\cdot}CH_2C(CH_3)_2OH + {}^{\cdot}CH_3 \longrightarrow CH_3CH_2C(CH_3)_2OH \quad (13)$$

$$2\,{}^{\cdot}CH_2C(CH_3)_2OH \longrightarrow (CH_3)_2C(OH)CH_2CH_2C(CH_3)_2OH \quad (14)$$

proposed. Since photoirradiation in D_2O gave a 1:0.41 CH_3D–CH_4 mixture in contrast to almost exclusive formation of D_2,

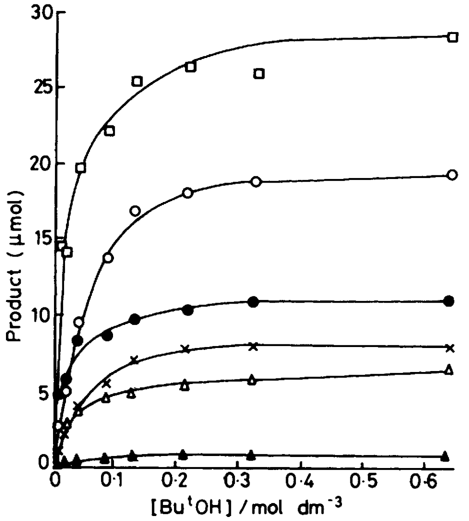

Figure 5. Influence of the concentration of Bu^{t}OH on the product yields. Symbols are same as in Figure 1

hydrogen abstraction of $^{\bullet}CH_3$ from Bu^{t}OH [reaction (15)]

$$(CH_3)_3COH + {}^{\bullet}CH_3 \longrightarrow {}^{\bullet}CH_2C(CH_3)_2OH + CH_4 \quad (15)$$

would also occur competitively with reaction (11). This implies that the TiO_2–Pt-catalysed photoreaction of Bu^{t}OH proceeds in part by radical-chain mechanism. The elementary reactions described above are consistent with the net reactions (1)—(4).

Since the photogenerated e can readily reduce O_2 to $O_2^{-\bullet}$,[15–18] the photocatalytic formation of H_2 [reaction (6)] and hence that of CH_4 [reaction (11)] will be quenched in the presence of O_2. Similarly, the scavenging of $^{\bullet}CH_2C(CH_3)_2OH$ intermediate by O_2 accounts for the decreased yield of 2,5-DH and Pn^{t}OH, although it is less efficient than that of e. On the other hand, the enhanced formation of acetone in the presence of O_2 is attributable to the photocatalytic oxygenation of the possible intermediate 2-methylprop-1-ene,[19–21] which was detected by mass spectrometry in the present photoreaction system [equation (16)].

$$CH_3C(CH_3)_2OH \xrightarrow[TiO_2]{-H_2O} CH_2{=}C(CH_3)_2 \xrightarrow[h\nu]{O_2,\ TiO_2}$$
$$\overline{OCH_2C(CH_3)_2O}) \longrightarrow (CH_3)_2CO + H_2C{=}O \quad (16)$$

As for O_2, Ag^+ ion can be a good electron acceptor, producing an Ag metal deposit on the TiO_2 surface.[9,10,14,22–24] Thus, the presence of Ag^+ ions inhibits H_2 formation almost completely in the TiO_2–Pt-catalysed photoreaction. Instead, the Ag^+ ions could convert the appreciable amount of Bu^{t}OH even with the use of anatase TiO_2 without Pt; the activity of rutile TiO_2 was considerably smaller (Table). Concerning the inhibition of the 2,5-DH formation, the redox reaction (17) may operate in contrast to the radical reaction by O_2.

$$^{\bullet}CH_2C(CH_3)_2OH + Ag^+ \longrightarrow (CH_3)_2CO + CH_3^+ + Ag \quad (17)$$

Influence of Bu^{t}OH *Concentration on the Photocatalytic Activity of* TiO_2–Pt.—Figure 5 illustrates variations of the product yields as a function of the concentration of Bu^{t}OH upon photoirradiation in 1M-NaOH solution with TiO_2–Pt under Ar. The yield of each product increased rapidly in the [Bu^{t}OH] range below 0.1M and then asymptotically approached a characteristic limiting value. As plotted in Figure 6, the Langmuir-type equation (18) can reproduce the data for the

$$Y = \alpha\beta[\mathrm{Bu^tOH}]/(1 + \alpha[\mathrm{Bu^tOH}]) \quad (18)$$

Bu^{t}OH concentration dependence where Y is the overall reaction yield, which is defined by the total number of moles of $2 \times H_2 + CH_4$ in the light of the relationship in Figure 3, α is the adsorption equilibrium constant, and β is the limiting reaction yield at [Bu^{t}OH] $\longrightarrow \infty$. The linear relationship in Figure 6 provided α 44 l mol^{-1} and β 65 μmol.

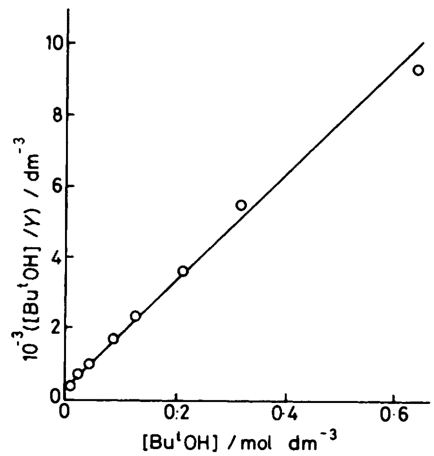

Figure 6. Linear plot of [Bu^{t}OH]/Y *versus* [Bu^{t}OH]

Thus, the amount of Bu^{t}OH$_{ads}$ is suggested to increase upon increasing the concentration of Bu^{t}OH, thereby undergoing hydrogen abstraction by $^{\bullet}OH_{ads}$ more efficiently. It is also likely that the reaction of Bu^{t}OH$_{ads}$ interrupts the deactivation of $^{\bullet}OH_{ads}$ to give a surface hydroxy group ($\equiv$Ti–OH) by e, *i.e.* delayed charge recombination between h^+ and e.

Concerning product distribution with varying concentrations of Bu^{t}OH, Figure 5 indicates that the yield of 2,5-DH becomes *ca.* 2-fold greater than that of acetone, although the latter exceeds the former in the [Bu^{t}OH] range <20mM. This result may be interpreted in terms of the enhanced bimolecular combination of the intermediate $^{\bullet}CH_2C(CH_3)_2OH_{ads}$ on the TiO_2 surface [reaction (4)]; $^{\bullet}CH_2C(CH_3)_2OH_{ads}$ at lower surface density would undergo β-scission to acetone and $^{\bullet}CH_3$ [reaction (10)] in preference to combination.

Reaction of Bu^{t}OH *by Hydroxyl Radical.*—We assume that the TiO_2–Pt-catalysed photoreaction of Bu^{t}OH involves formation of $^{\bullet}OH_{ads}$ and hydrogen abstraction from Bu^{t}OH$_{ads}$ on the TiO_2 surface. In order to characterize the reactivity of $^{\bullet}OH$ toward Bu^{t}OH in homogeneous aqueous solution, we also carried out the γ-radiolysis under N_2O, and the reaction with Fenton's reagent. The primary active species in the dilute aqueous solution system (pH 7.0) are derived from radiolysis of water by reaction (19) where the G values are the number of

$$H_2O \xrightarrow{\gamma} {}^{\bullet}OH\ (G\ 2.7) + H^{\bullet}\ (G\ 0.55) + e_{aq}\ (G\ 2.7) \quad (19)$$

molecules produced per 100 eV of energy absorbed by the solution. The presence of excess of N_2O converts the hydrated electron (e_{aq}) into $^{\bullet}OH$ [reaction (20)]. Thus, the γ-radiolysis of

$$e_{aq} + N_2O \longrightarrow {}^{\bullet}OH + OH^- + N_2 \quad (20)$$

N_2O-saturated solution produces $^{\bullet}OH$ (G 5.4) along with minor amounts of $H^{\bullet}$ (G 0.55).[25]

It is evident from the Table that both the homogeneous $^{\bullet}OH$ reaction systems give a product distribution similar to the TiO_2–Pt-catalysed photoreaction system. This result provides a strong indication of the generation of $^{\bullet}OH$, probably in the adsorbed form $^{\bullet}OH_{ads}$, by the photoirradiation of TiO_2. Also notable is the fact that γ-radiolysis under N_2O showed less pH dependence compared with the photocatalytic reaction (Table); the reaction with Fenton's reagent proceeded only under acidic conditions ($pH < 2.0$). It is likely that modification of the TiO_2 surface, protonation and deprotonation of the hydroxy groups as regulated by the pH of aqueous solution phase,[26] is among the major determinants of the photocatalytic activity of TiO_2–Pt.

In summary, this paper has characterized the behaviour of Bu^tOH in aqueous systems with the photoirradiated TiO_2–Pt catalyst. $^{\bullet}CH_2C(CH_3)_2OH$ is the most probable intermediate derived from hydrogen abstraction from Bu^tOH by photogenerated $^{\bullet}OH_{ads}$, undergoing bimolecular combination and β-scission competitively.

References

1 A. J. Bard, *J. Photochem.*, 1979, **10**, 59; *Science*, 1980, **207**, 139.
2 A. J. Nozik, *Annu. Rev. Phys. Chem.*, 1978, **29**, 189.
3 M. S. Wrighton, *Acc. Chem. Res.*, 1979, **12**, 303.
4 S. Nakabayashi, A. Fujishima, and K. Honda, *Chem. Phys. Lett.*, 1983, **102**, 464.
5 T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, 1980, 694.
6 P. Pichat, J.-M. Herrmann, J. Disdier, H. Courbon, and M.-N. Mozzanega, *Nouv. J. Chim.*, 1981, **5**, 627.
7 S. Teratani, J. Nakamichi, K. Taya, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1688.
8 K. Domen, S. Naito, T. Ohnishi, and K. Tamaru, *Chem. Lett.*, 1982, 555.
9 S. Nishimoto, B. Ohtani, A. Sakamoto, and T. Kagiya, *Nippon Kagaku Kaishi*, 1984, 246.
10 S. Nishimoto, B. Ohtani, H. Kajiwara, and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 61.
11 S. Nishimoto, B. Ohtani, H. Shirai, and T. Kagiya, *J. Polym. Sci., Polym. Lett. Edn.*, 1985, **23**, 141.
12 S. Nishimoto, B. Ohtani, and T. Kagiya, in N. S. Allen and J. F. Rabek, 'New Trends in Polymer Photochemistry,' Applied Science, London, 1985, p. 289.
13 S. Arimitsu, T. Imafuku, and I. Shiojima, Symposium on Photochemistry, Japan, IIIA-301, 1980; Jap. P. 57 35525.
14 S. Nishimoto, B. Ohtani, H. Kajiwara, and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2685.
15 R. I. Bickley, G. Munuera, and F. S. Stone, *J. Catal.*, 1973, **31**, 398.
16 R. I. Bickley and R. K. M. Jayanty, *Faraday Discuss. Chem. Soc.*, 1974, **58**, 194.
17 R. B. Cundall, R. Rudham, and M. S. Salim, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1642.
18 P. R. Harvey, R. Rudham, and S. Ward, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 1381.
19 N. Djeghri, M. Formenti, F. Juillet, and S. J. Teichner, *Discuss. Chem. Faraday Soc.*, 1974, **58**, 185.
20 I. Carrisoza and G. Munuera, *J. Catal.*, 1977, **49**, 174.
21 I. Carrisoza and G. Munuera, *J. Catal.*, 1977, **49**, 189.
22 E. Borgarello, J. Kiwi, M. Gratzel, E. Pellizzeti, and M. Visca, *J. Am. Chem. Soc.*, 1982, **104**, 2996.
23 P. D. Fleischauer, H. K. Alen Kan, and J. R. Schepherd, *J. Am. Chem. Soc.*, 1972, **94**, 283.
24 A. W. Adamson and P. D. Fleischauer, 'Concepts of Inorganic Photochemistry,' Wiley, New York, 1975, p. 400.
25 H. A. Schwarz, *J. Chem. Educ.*, 1981, **58**, 101.
26 H. P. Boehm, *Discuss. Faraday Soc.*, 1971, **52**, 264.

Received 11*th February* 1985; *Paper* 5/243