Photocatalytic Dehydrogenation of Aliphatic Alcohols by Aqueous Suspensions of Platinized Titanium Dioxide

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Photoirradiation ($\lambda_{ex} > 300$ nm) of Ar-purged aqueous propan-2-ol solution gave hydrogen and acetone in the presence of platinum- and/or ruthenium dioxide-loaded TiO_2. The photocatalytic activity of anatase TiO_2 depended significantly on the amount of metal or metal oxide present; the effect on the activity increased in the order platinum black $\gg$ platinum powder > ruthenium dioxide. The photocatalytic activity of rutile TiO_2 was negligible even when loaded with platinum black. The effective wavelengths for the photocatalytic dehydrogenation of propan-2-ol were below *ca.* 390 nm, in agreement with the u.v. absorption spectrum of anatase TiO_2. In a similar way primary, secondary and tertiary aliphatic alcohols underwent photocatalytic oxidation, accompanied by hydrogen liberation, by the platinized TiO_2. The primary and secondary alcohols gave the corresponding carbonyl derivatives, while 2-methylpropan-2-ol and acetone gave dimeric products accompanied by stoichiometric hydrogen evolution. The initial rate of dehydrogenation in these photocatalytic systems was in proportion to the rate constants of hydrogen abstraction by hydroxyl radical in the homogeneous systems.

A common feature of semiconductor photocatalysts is that they generate electron–hole pairs when irradiated with light of energy greater than their band gaps.[1] Although the importance of electrons and holes as the primary active species in photocatalytic reactions has been recognized, the mechanism of their action is still a subject of considerable controversy.

Many authors have reported the photocatalytic reactions of alcohols[2-9] by platinized titanium dioxide (TiO_2/Pt). They discussed the photocatalytic activity of TiO_2 and the effect of metal loading. However, few investigations[3,10] have been reported on the reactivity of alcohols which are oxidized on the photoirradiated semiconductor particles.

In the present work the photocatalytic reaction of a series of primary, secondary and tertiary aliphatic alcohols by platinized TiO_2 powder is reported. The correlation of the initial oxidation rate in aqueous suspension with the corresponding rate constant of hydrogen abstraction by hydroxyl radicals in a homogeneous system is discussed.

EXPERIMENTAL

MATERIALS

Titanium dioxide powder (anatase $> 99\%$; SO_4^{2-}, 0.05%; Cl^-, 0.01%) was supplied by Merck and used without further activation. Rutile TiO_2 powder was prepared by calcination of anatase at 1200 °C for 10 h in an electric furnace. This treatment transformed almost all the crystals into rutile (as determined by X-ray diffraction analysis, described elsewhere[11]). Platinum [Pt black (Nakarai Chemicals) or Pt powder (Higuchi Chemical laboratory), 5 wt %] or ruthenium

dioxide [RuO$_2$ (Nakarai Chemicals), 10 wt %] was mixed with TiO$_2$ powder in an agate mortar to prepare the catalyst.[5, 12–15] The catalysts thus prepared showed reproducibility within ± 10% for the photocatalytic reaction. Water used in these experiments was purified by distillation after passage through an ion-exchange resin. Acetone and the aliphatic alcohols were used without further purification.

PHOTOIRRADIATION

The powdered catalyst (50 mg) was suspended in an aqueous solution (5.0 cm^3) of the substrate (0.50 mmol) under neutral or alkaline (6 mol dm^{-3} NaOH) conditions in a glass tube (15 mm in diameter and 180 mm in length, transparent to light of wavelength > 300 nm). The magnetically stirred solution under Ar was irradiated at > 300 nm using a merry-go-round apparatus equipped with a 400-W high-pressure mercury arc (Eiko-sha 400).

MONOCHROMATIC PHOTOIRRADIATION

In the quantum-yield measurements 30 mg of the platinized TiO$_2$ powder and 4.0 cm^3 of 6 mol dm^{-3} NaOH solution were placed in a rectangular quartz cell (1.0 cm path-length) with a Pyrex finger (10 mm in diameter and ca. 15 cm in length) and purged with Ar. The suspension was irradiated by a Philips SP 500 ultra-high-pressure mercury arc (operated at 750 W) through a grating monochromator (Jasco CT 25N). The number of photons incident upon the suspension through the monochromator and the quartz cell was evaluated by ferric oxalate actinometry.[16] In the present system the formal quantum efficiency was evaluated as the ratio of twice the number of hydrogen atoms evolved to the number of incident photons, rather than the number of absorbed photons, because of the difficulty in measuring the exact number of photons absorbed by TiO$_2$ particles. Hence the true efficiency should be larger than the efficiency reported in fig. 1.

The ultraviolet absorption spectrum of TiO$_2$ was recorded on a Hitachi EPS-3T spectrophotometer equipped with an R-10A integrating sphere.

PRODUCT ANALYSIS

After irradiation the gas phase of the sealed sample was analysed by gas chromatography (g.c.).[11] The suspension was centrifuged to filter off the catalyst and the solution was subjected to product analysis by g.c. under conditions described previously.[11] The amount of 2,5-dimethylhexane-2,5-diol present was also determined by g.c. with a Tenax GC column (3 mm in diameter and 1 m in length) at 200 °C. Formaldehyde was determined by a modified acetylacetone (pentane-2,4-dione) method. A portion of the aqueous sample containing formaldehyde was mixed with an aqueous solution of pentane-2,4-dione and ammonium chloride.[17] The resulting yellow derivative, 1,4-dihydro-3,5-diacetyl-2,6-lutidine was extracted with chloroform and subjected to u.v. absorption measurements ($\lambda_{max} \approx 396$ nm) with a Shimadzu UV-200S spectrophotometer.

RESULTS AND DISCUSSION

PHOTOCATALYTIC ACTIVITY OF PLATINUM- AND/OR RUTHENIUM DIOXIDE-LOADED TiO$_2$ POWDERS FOR PROPAN-2-OL DEHYDROGENATION

Table 1 shows the hydrogen yield for the photocatalytic reaction of propan-2-ol in the presence of platinum- and/or ruthenium dioxide-loaded TiO$_2$ suspension under deaerated conditions. Although the activities of both anatase and rutile TiO$_2$ without loaded metal were negligible in neutral and in alkaline solutions, a small amount of metal on the TiO$_2$ surface enhanced the activity of anatase, e.g. only 5 wt% of platinum black loading enhanced the activity by ca. 100-fold under both neutral and alkaline conditions. Pt powder and RuO$_2$ were also effective for photocatalytic hydrogen formation, but the effects on the activity enhancement were small compared with platinum black.

These modified anatase systems also produced acetone, whose yield was almost equal to that of hydrogen and to the consumption of propan-2-ol, showing that dehydrogenation of propan-2-ol proceeds photocatalytically [see also reaction (3)

Table 1. Photocatalytic dehydrogenation of propan-2-ol by aqueous suspensions of anatase and rutile loaded with Pt and/or RuO_2[a]

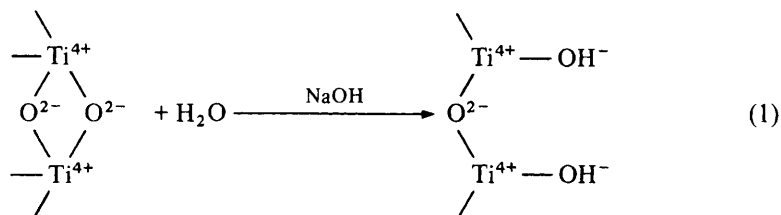| run	catalyst[b]	in H_2O		in 6 mol dm^{-3} NaOH
		H_2	acetone	H_2/μmol
1	$TiO_2(A)$	0.7	1.6	2.6
2	$TiO_2(A)$ + Pt powder (5%)	13	11	38
3	$TiO_2(A)$ + Pt black (5%)	93	79	200
4	$TiO_2(A)$ + RuO_2 (10%)	8.9	9.0	30
5	$TiO_2(A)$ + Pt black (5%) + Ruo_2 (10%)	130	132	210
6	$TiO_2(R)$	0.1	0.6	1.3
7	$TiO_2(R)$ + Pt black (5%)	0.4	4.3	2.4

[a] Catalyst (50 mg), NaOH aqueous solution (6 mol dm^{-3}, 5.0 cm^3) and propan-2-ol (38 mm^3, 500 μmol) were irradiated with 500-W high-pressure mercury arc under Ar at room temperature.
[b] $TiO_2(A)$ and $TiO_2(R)$ refer to anatase and rutile.

later].[5,14,15] The enhanced activity of the TiO_2 loaded with platinum black is accounted for by the facilitated reduction of H^+, or H_2O under alkaline conditions, on the metal surface,[18,19] which increases the efficiency of charge separation of the photogenerated electron (e^-) – hole (h^+) pair,[1] as is also the case for RuO_2.[20] The smaller enhancement by platinum powder may be due to its poor contact with TiO_2, since the crystallite size of the platinum powder was of the same order of magnitude (> 200 nm) as that of anatase, while that of platinum black is ca. 6 nm as evaluated from X-ray diffraction.

On the other hand, the activity of rutile was negligible even when loaded with platinum black. Rutile with a particle size larger than that of anatase has been reported to show similar or even greater activity for the photodeposition of Ag metal compared with anatase. This is a strong indication that the efficiencies of anatase and rutile in photochemically producing electron–hole pairs are of the same order. Therefore, the small activity of rutile for H_2 formation is attributable to the disadvantageous energy of the photogenerated electron.[14,15,21]

The effect of adding a base was evident in the present systems, as reported previously;[22] a 1.5–3-fold increased amount of hydrogen was obtained compared with the neutral solution (see table 1). Although there is no structural evidence at present, the surface modification induced by the alkaline treatment may account for this enhancement [see reaction (1)]. An increase in the specific surface area and in the amount of surface hydroxyl groups accompanying the alkaline treatment has been reported:[23]

$$\begin{array}{c} \diagdown \\ -Ti^{4+} \\ \diagup \diagdown \\ O^{2-} \quad O^{2-} \quad + H_2O \xrightarrow{\text{NaOH}} \\ \diagdown \diagup \\ -Ti^{4+} \\ \diagup \end{array} \qquad \begin{array}{c} \diagdown \\ Ti^{4+} - OH^- \\ \diagup \\ O^{2-} \\ \diagdown \\ Ti^{4+} - OH^- \\ \diagup \end{array} \qquad (1)$$

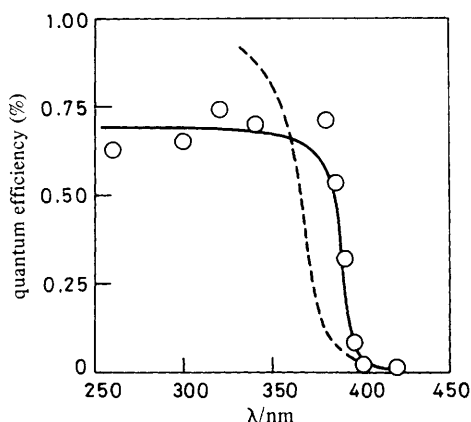The surface hydroxyl is expected to be a hole-trapping site, as discussed in the next section.

Fig. 1. Variation in quantum efficiency of the photocatalytic dehydrogenation of propan-2-ol in a TiO_2/Pt suspension under Ar as a function of the wavelength of monochromatic light. The broken line represents the absorption spectrum of the TiO_2 suspension.

WAVELENGTH DEPENDENCE OF PROPAN-2-OL DEHYDROGENATION BY SUSPENDED PLATINIZED TiO_2 CATALYST

Fig. 1 shows the dependence of the formal quantum efficiency of the photocatalytic dehydrogenation of propan-2-ol on the irradiation wavelength. The anatase powder loaded with platinum black (TiO_2/Pt) was used as a photocatalyst and 6 mol dm^{-3} NaOH solution as solvent. The efficiency over the wavelength range 260–380 nm was apparently constant (0.6–0.8%) and decreased drastically at the longer wavelengths of *ca.* 380–400 nm. Photoirradiation at wavelengths > 400 nm produced negligible amounts of hydrogen. The observed action spectrum of anatase reasonably corresponds to the absorption spectrum shown in fig. 1. These facts indicate that propan-2-ol dehydrogenation is initiated by the photoexcitation of an electron from the valence band into the conduction band with light of energy greater than the band gap [*ca.* 3.2 eV (corresponding to *ca.* 390 nm) for anatase TiO_2].[21]

INFLUENCE OF PROPAN-2-OL CONCENTRATION

The initial rate of H_2 formation [$r(H_2)$] by the TiO_2/Pt photocatalyst was measured as a function of the initial concentration of propan-2-ol (C). A sharp increase in $r(H_2)$ was observed on increasing C to 100 mmol dm^{-3}. In the higher-C region $r(H_2)$ was practically constant (*ca.* 3.5 μmol h^{-1}). Plots of these data according to a Langmuir adsorption isotherm, $1/r(H_2) = f(1/C^n)$ ($n = 1$ or $1/2$), are shown in fig. 2. A linear relation was obtained for $n = 1$ (molecular adsorption) rather than $n = 1/2$ (dissociative adsorption). Pichat and coworkers reported the dissociative adsorption of methanol onto the TiO_2 surface in the photocatalysis by platinized TiO_2,[3] on the basis of a linear relation for $n = 1/2$. Since the molecular adsorption of propan-2-ol[24] is more probable in the present system, the amount of adsorbed propan-2-ol is thought to determine the rate of overall reaction [see reaction (3) later], as discussed in the following section.

PHOTOCATALYSIS OF ALIPHATIC ALCOHOLS BY PLATINIZED TiO_2

Table 2 shows the results of the photocatalytic dehydrogenation of a series of aliphatic alcohols and acetone in the presence of TiO_2/Pt under neutral conditions. These reactions could not be observed in the dark, nor in the absence of TiO_2/Pt.
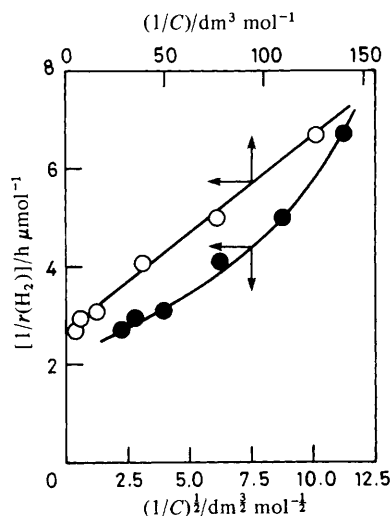
Fig. 2. Linear transform of the Langmuir equation of the rate of H_2 formation $[r(H_2)]$ and the propan-2-ol concentration (C): $[1/r(H_2)] = f(1/C^n)$ for $n = 1$ ($\bigcirc$) and $n = 1/2$ ($\bullet$). Irradiation was performed with a 500-W high-pressure mercury arc for 1.0 h.

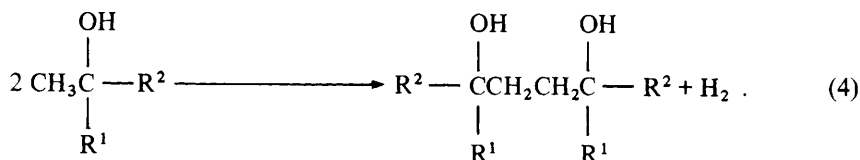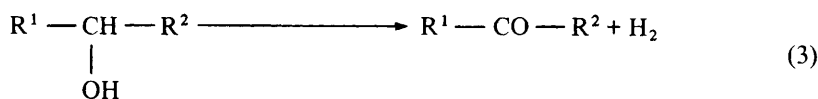**Table 2.** Photocatalytic dehydrogenation of alcohols and acetone by platinized $TiO_2{}^a$

substrate	$H_2/\mu mol$	organic product/μmol	
CH_3COCH_3	3.3	$(CH_3COCH_2—)_2$	5.9
$(CH_3)_3COH$	18	$[(CH_3)_2CH(OH)CH_2—]_2$	18
		CH_3COCH_3	1.6
CH_3OH	20	HCHO	14
$CH_2(OH)CH_2OH$	16	$HOCH_2CHO$	14
		CH_3CHO	5.3
CH_3CH_2OH	20	CH_3CHO	17
$(CH_3)_2CHOH$	54	CH_3COCH_3	46

^{a} The substrate (0.5 mmol) in water (5.0 cm³) was irradiated in the presence of platinized TiO_2 (50 mg) for 10 h under Ar at room temperature.

All the alcohols except 2-methylpropan-2-ol gave carbonyl products.[2,3] Similarly, ethylene glycol gave 2-hydroxyethanal. In the case of 2-methylpropan-2-ol a dimeric product 2,5-dimethylhexane-2,5-diol,[25] was obtained together with small amounts of acetone and 2-methylbutan-2-ol.[26] Acetone was less reactive and gave only a small amount of dimeric product, hexane-2,5-dione.

Evolution of H_2 was observed simultaneously in each system. It is clear from table 2 that the H_2 yield is virtually equal to that of the carbonyl and dimeric products derived from these alcohols. Thus the overall photocatalytic reaction of alcohols at the initial stage can be represented by

$$RCH_2OH \longrightarrow RCHO + H_2 \qquad (2)$$

$$R^1 - CH - R^2 \longrightarrow R^1 - CO - R^2 + H_2$$
$$\qquad\qquad | $$
$$\qquad\qquad OH \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)$$

$$\qquad OH \qquad\qquad\qquad\qquad\qquad\qquad OH \qquad OH$$
$$\qquad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \qquad\quad |$$
$$2\ CH_3C - R^2 \longrightarrow R^2 - CCH_2CH_2C - R^2 + H_2 \ . \qquad (4)$$
$$\qquad | \qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\quad |$$
$$\qquad R^1 \qquad\qquad\qquad\qquad\qquad\qquad\ R^1 \qquad R^1$$

The reactivity of the alcohols varies in the order secondary > primary > tertiary (table 2). This order agrees with that observed in the conventional oxidation of alcohols.

In fig. 3 the initial rate of H_2 evolution for the alcohol solutions (0.1 mol dm^{-3}) is plotted against the rate constant of hydrogen abstraction by hydroxyl radicals in aqueous solution.[27] The linear correlation in both neutral and alkaline solutions shows that the photocatalytic reactivity of the alcohols is similar to hydrogen abstraction in the dark.
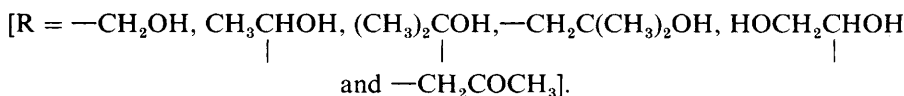
A possible mechanism for the dehydrogenation of the alcohols is as follows. In the presence of the Pt-loaded catalyst, reduction of H^+ by the photoexcited electron to produce H_2 proceeds readily because of the small activation energy needed to release H_2 from the Pt surface. However, in the absence of reductants such as alcohols, recombination of the hole and the electron leads to a negligible liberation of H_2. Thus the photocatalytic reaction strongly depends on the oxidation step induced by the photogenerated positive hole. A similar mechanism was also suggested by Dunn and coworkers.[28,29]

The quantum efficiency can be approximately expressed in terms of the efficiency of the oxidation of the adsorbed alcohol (k_{ox}[ROH]) and that of electron–hole recombination (k_d),

$$\Phi = f k_{ox}[ROH]/(k_d + k_{ox}[ROH]) \qquad (5)$$

where f denotes the efficiency of photoexcitation ($0 < f < 1$). Under conditions where $\Phi \ll 1$, i.e. $k_d \gg K_{ox}[ROH]$, Φ is approximately proportional to $k_{ox}[ROH]$. Furthermore, on the assumption that the effective concentration of alcohol ([ROH]) is identical (i.e. with alcohol the TiO_2 surface is almost saturated, see fig. 2), the rate of H_2 evolution, which is directly proportional to Φ, should be approximately proportional to the rate constant of oxidation of the alcohol (k_{ox}).

Accordingly, the linear relations shown in fig. 3 strongly suggest that the alcohol oxidation proceeds via hydrogen abstraction from the alcohol molecule. Many researchers suggested the intermediacy of a hydroxyl radical adsorbed on the TiO_2 surface, which is produced by the reaction of a hole:[3,5,7,15,26,30,31]

$$RH + {}^{\cdot}OH_{ads} \rightarrow {}^{\cdot}R + H_2O \qquad (6)$$

$$[R = -CH_2OH,\ CH_3CHOH,\ (CH_3)_2COH, -CH_2C(CH_3)_2OH,\ HOCH_2CHOH$$
$$\qquad\qquad\qquad | \qquad\qquad\qquad\qquad | \qquad\qquad\qquad\qquad |$$
$$and\ -CH_2COCH_3].$$

In the case of the primary and secondary alcohols the hydroxyalkyl radicals undergo further oxidation via hydrogen abstraction to carbonyl derivatives:
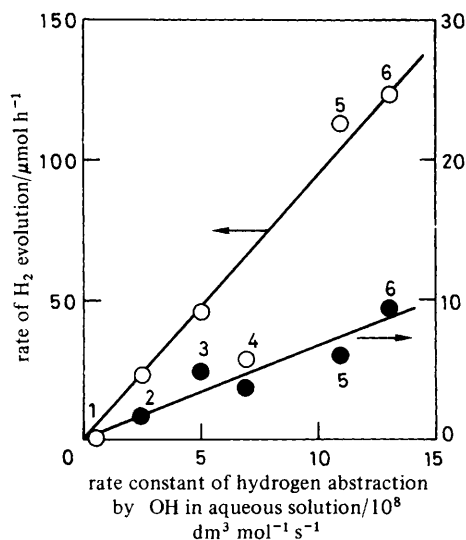
$$R^1R^{2\cdot}COH + {}^{\cdot}OH_{ads} \rightarrow R^1R^2C{=}O + H_2O. \qquad (7)$$
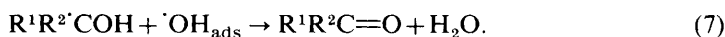
Fig. 3. Hydrogen evolution rate as a function of the rate constant of hydrogen abstraction by hydroxyl radical in aqueous solution.[25] The substrate (500 μmol) and TiO_2/Pt (platinum black, 5 wt %, 50 mg) were placed in 5.0 cm^3 of water (●) and 6 mol dm^{-3} NaOH solution (○), and irradiated by a 400-W high-pressure mercury arc for 2.5 and 0.5 h, respectively. (1) Acetone, (2) 2-methylpropan-2-ol, (3) methanol, (4) ethylene glycol, (5) ethanol and (6) propan-2-ol.

Radicals produced from 2-methylpropan-2-ol and acetone, both of which bear no α-hydrogen, predominantly undergo recombination into dimeric derivatives. In the light of the results shown in fig. 3, the steps leading to the final products proceed more efficiently than the primary step, *i.e.* hydrogen abstraction.

[1] (a) A. J. Nozik, *Annu. Rev. Phys. Chem.*, 1978, **29**, 189; (b) M. S. Wrighton, *Acc. Chem. Res.*, 1979, **12**, 303; (c) A. J. Bard, *J. Photochem.*, 1979, **10**, 59; *Science*, 1980, **207**, 139; *J. Phys. Chem.*, 1982, **86**, 172.

[2] T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, 1980, 694.

[3] P. Pichat, J-M. Herrmann, J. Disdier, H. Courbon and M-N. Mozzanega, *Nouv. J. Chim.*, 1981, **5**, 627.

[4] S. Teratani, J. Nakamichi, K. Taya and K. Tanaka, *Bull. Chem. Soc. Jpn*, 1982, **55**, 1688.

[5] S. Nishimoto, B. Ohtani, H. Shirai and T. Kagiya, *J. Polym. Sci., Polym. Lett. Ed.*, 1985, **23**, 141.

[6] S. Nishimoto, B. Ohtani and T. Kagiya, in *New Trends in Polymer Photochemistry*, ed. N. S. Allen and J. F. Rabek (Applied Science Publishers, London, 1985), in press.

[7] H. Harada and T. Ueda, *Nouv. J. Chim.*, 1984, **8**, 123.

[8] F. H. Hussein and R. Rudham, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2817.

[9] S. Davidson, C. L. Morrison and J. Abraham, *J. Photochem.*, 1984, **24**, 27.

[10] T. Kawai, T. Sakata, K. Hashimoto and M. Kawai, *Nippon Kagaku Kaishi*, 1984, 277.

[11] S. Nishimoto, B. Ohtani, H. Kajiwara and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2685.

[12] T. Kawai and T. Sakata, *Nature (London)*, 1980, **286**, 474.

[13] S. Nishimoto, B. Ohtani, T. Yoshikawa and T. Kagiya, *J. Am. Chem. Soc.*, 1983, **105**, 7180.

[14] S. Nishimoto, B. Ohtani, A. Sakamoto and T. Kagiya, *Nippon Kagaku Kaishi*, 1984, 246.

[15] S. Nishimoto, B. Ohtani, H. Kajiwara and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 61.

[16] C. G. Hachard and C. A. Parker, *Proc. R. Soc. London A*, 1956, **235**, 518.

[17] (a) T. Nash, *Biochem. J.*, 1953, **55**, 416; (b) Japan Industrial Standard, K 0102, 1974.

[18] S. Nakabayashi, A. Fujishima and K. Honda, *Chem. Phys. Lett.*, 1983, **102**, 464.

[19] J. Disdier, J-M. Herrmann and P. Pichat, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 651.

[20] T. Sakata, K. Hashimoto and T. Kawai, *J. Phys. Chem.*, 1984, **88**, 5214.

[21] B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 2239, 5985.
[22] T. Kawai and T. Sakata, *Chem. Lett.*, 1981, 81.
[23] S. Okazaki and T. Kanto, *Nippon Kagaku Kaishi*, 1976, 404.
[24] P. R. Harvey, R. Rudham and S. Ward, *J. Chem. Soc.*, *Faraday Trans. 1*, 1983, **79**, 2975.
[25] Sagami Chemical Research Center, Japan, p. 57 35525; *Chem. Abst.*, **97**: 38481y.
[26] S. Nishimoto, B. Ohtani, H. Shirai and T. Kagiya, *J. Chem. Soc.*, *Perkin Trans. 2*, submitted for publication.
[27] M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isot.*, 1967, **18**, 493.
[28] W. W. Dunn, Y. Aikawa and A. J. Bard, *J. Am. Chem. Soc.*, 1981, **103**, 3456.
[29] W. W. Dunn, Y. Aikawa and A. J. Bard, *J. Electrochem. Soc.*, 1981, **128**, 222.
[30] R. B. Cundall, R. Rudham and M. S. Salim, *J. Chem. Soc.*, *Faraday Trans. 1*, 1976, **72**, 1642.
[31] P. R. Harvey, R. Rudham and S. Ward, *J. Chem. Soc.*, *Faraday Trans. 1*, 1983, **79**, 1381.

(PAPER 4/2138)