ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 108 (1997) 55–58

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photocatalytic degradation of 1,4-dioxane in aqueous solution

Roger R. Hill *, Graham E. Jeffs, David R. Roberts

Department of Chemistry, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK

Received 19 April 1996; accepted 23 July 1996

Abstract

1,4-Dioxane is readily mineralized by the photocatalytic action of TiO_2 via an accumulation and slower degradation of ethylene diformate.

Keywords: Aqueous solution; 1,4-Dioxane; Photocatalytic degradation

1. Introduction

The widely used solvent, 1,4-dioxane, is a known toxic hazard [1], its potential adventitious occurrence in cosmetic products prompting recent efforts to improve methods of assay [2]. However, physical removal from industrial intermediates only defers the disposal problem which, with high dilutions, is economically significant. The general ineffectiveness of bioreactors and other treatment options has encouraged not only the search for improved microbiological performance [3], but also efforts to enhance degradation by prior oxidation with hydrogen peroxide and ozone [4]. The rapidly expanding field of photocatalytic detoxification [5] may offer alternative solutions to such problems but, to our knowledge, no detailed study has been made of its application to 1,4-dioxane. However, the action of light, air and titanium dioxide on the closely related morpholine has been found to promote efficient degradation through multiple pathways [6].

We have found that 1,4-dioxane is effectively mineralized in aqueous solution by the combined action of light ($\lambda > 300$ nm), air and TiO_2; this involves the growth and decay of ethylene diformate as the most significant observable intermediate. The analogous pathway is not evident in the products reported for morpholine degradation.

2. Experimental details

1,4-Dioxane and all other chemicals, except TiO_2 (Degussa P25), were supplied by Sigma Aldrich Co., Limited. 1,4-Dioxane was further purified by elution through activated alumina.

2.1. High performance liquid chromatography (HPLC) analyses

Photolysates were monitored by sample filtration through a Gelman LC13 0.2×10^{-6} m filter before analysis using a system comprising a Waters 712 Wisp autoinjector, a Milton Roy LDC 3000 pump, a 250 mm×4.6 mm (5×10^{-6} m particle) PLRPS column, a Milton Roy LDC 3100 UV detector at 200 nm and a Waters 740 computing integrator, with 6% acetonitrile in water as the mobile phase. Analyses for formic, acetic, glycolic and glyoxylic acids, formaldehyde and acetaldehyde were performed using coupled 140 mm×4.1 mm PRP1 and 220 mm×4.6 mm Polypore H columns with 0.025 mol dm^{-3} H_2SO_4 as the mobile phase.

2.2. Carbon dioxide

CO_2 was determined by headspace analysis in the photochemical reactor, 0.5 cm^3 samples being removed through a Subaseal with an SGE gas-tight syringe with integral on/off valve. The samples were analysed with a Pye 204 gas chromatograph fitted with an Alltech CTR column and thermal conductivity detector, using 3.04% and 10.1% CO_2 external standards supplied by Phase Separations, Limited.

2.3. Photolyses

Experiments were conducted with a Rayonet multilamp reactor and repeated in an Applied Photophysics immersion well apparatus. The Rayonet reactor, fitted with 350 nm lamps

---

* Corresponding author.

1010-6030/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved
PII S1010-6030(96)04463-2

and a borosilicate cylindrical reaction vessel, flanged with a multiport lid, was charged with 800 cm^3 6.4×10^{-3} mol dm^{-3} dioxane in water and 0.9 g P25 TiO_2, leaving a head-space of 800 cm^3. The vessel was thoroughly purged with oxygen at the start and following the removal of gas and liquid samples. The suspension was agitated at room temperature with a magnetic stirrer and a cold finger condenser was inserted in one of the ports.

The Applied Photophysics immersion well reactor was fitted with a 400 W medium-pressure mercury arc, a Pyrex inner thimble and a water-cooled jacket. The vessel was charged with 400 cm^3 of solution and 0.4 g P25 TiO_2; the suspension was purged continuously with CO_2-free air and the outflow was collected in Tedlar gas bags fitted with Omnifit Subaseal sampling ports. Liquid samples were also taken from the reaction vessel through an Omnifit Subaseal.

2.4. *Isolation and characterization of ethylene diformate*

Irradiation of P25 TiO_2 (0.8 g) in 0.2% aqueous 1,4-dioxane (400 cm^3) was carried out in the Applied Photophysics apparatus until more than 80% dioxane had reacted. After low vacuum filtration through 6 mm Celite 575 on a Grade 3 sinter, the total volume was reduced to 35 cm^3 by evaporation and extracted in five portions with $CDCl_3$ (3 cm^3). After drying with anhydrous calcium chloride, the $CDCl_3$ solution was examined by HPLC, IR and NMR spectroscopy which afforded data fully consistent with ethylene diformate [7]: $\nu_{max} = 1725$ cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.05 (2H, s, DEPT CH), 4.38 (4H, s, DEPT CH_2); ^{13}C NMR ($CDCl_3$) δ: 161.6 (off-res. d), 61.2 (off-res. t).

3. Results

Fig. 1 shows the progress of the photocatalysed degradation of aqueous 1,4-dioxane carried out in a Rayonet reactor up to the release of 70% of the theoretical amount of carbon dioxide. The relationship between the loss of substrate, growth and decay of the dominant peak in the high performance liquid chromatogram of the photolysate and the growth of CO_2 was reproduced after 5 h by photolysis using an Applied Photophysics immersion well reactor. The latter reaction had released more than 91% of the theoretical amount of CO_2 when the irradiation was terminated after a further 20 h. The intermediate was found to be ethylene diformate (see Section 2).

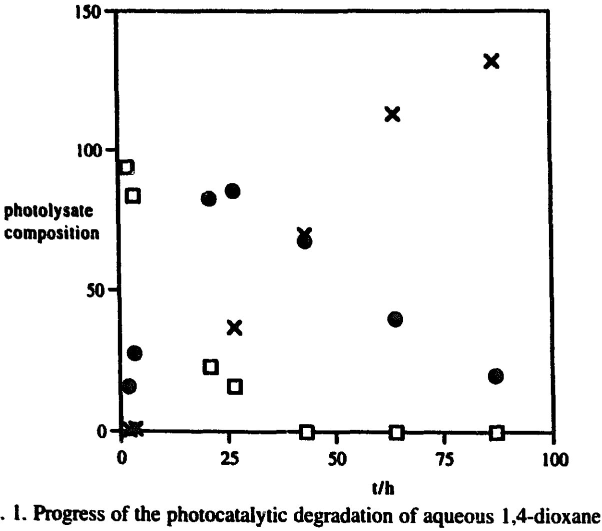


Fig. 1. Progress of the photocatalytic degradation of aqueous 1,4-dioxane: 1,4-dioxane, per cent original concentration (□); CO_2, mol × 10^4 (×); ethylene diformate, HPLC peak area (●).

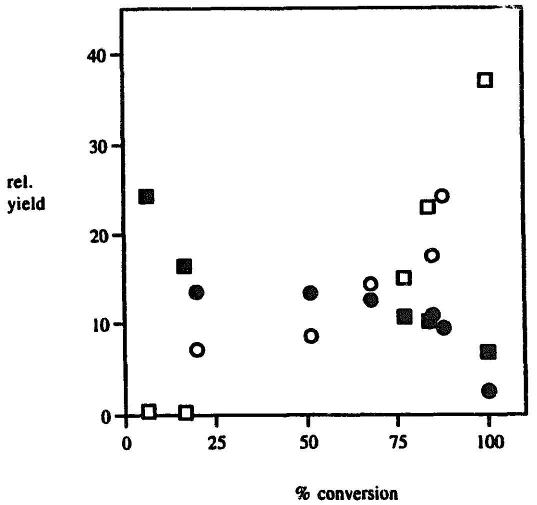


Fig. 2. Variation in the relative yields with reference to photocatalytically oxidized 1,4-dioxane: CO_2 (per cent of theoretical), Rayonet (□), Applied Photophysics (○); ethylene diformate (HPLC area/per cent dioxane converted), Rayonet (■), Applied Photophysics (●).

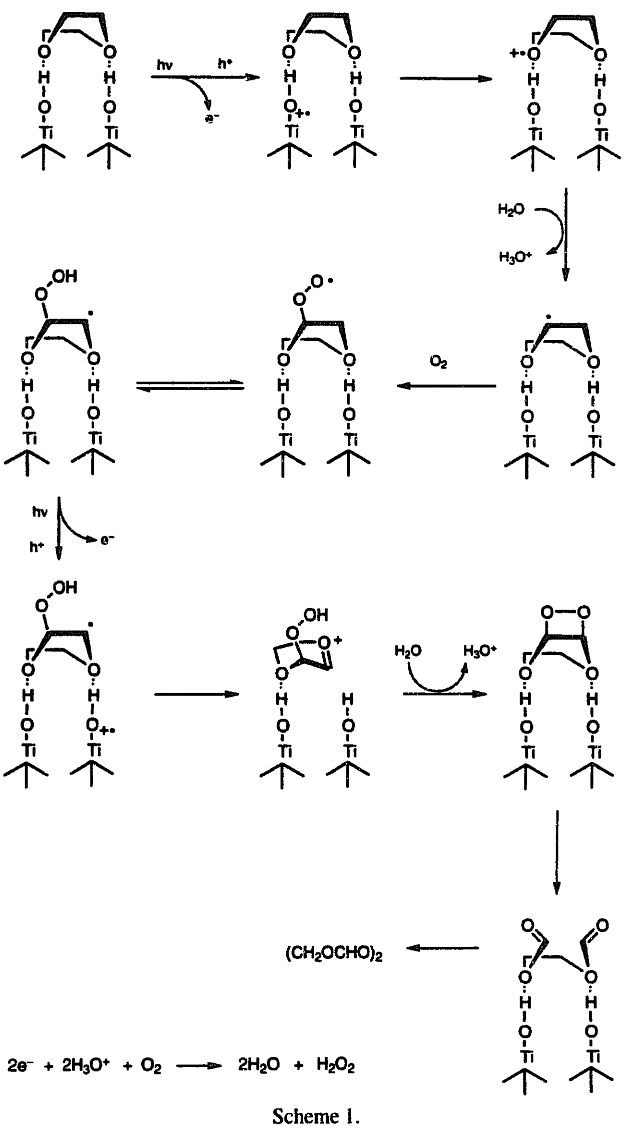
No reaction was observed if any one of the components, oxygen, UV radiation or TiO_2, was omitted. HPLC procedures which detect other possible intermediates, e.g. glycolic, glyoxylic, acetic and formic acids, acetaldehyde and formaldehyde, failed to do so at all stages of photolysis examined, with the exception of formic acid in almost completely reacted samples.

Fig. 2 shows combined data from Rayonet and Applied Photophysics photolyses which demonstrate how the yields of ethylene diformate and CO_2 are related to the consumption of the substrate. The typical "secondary" behaviour expected for CO_2 is evident, whereas ethylene diformate appears, in this sense, to be a "primary" product.

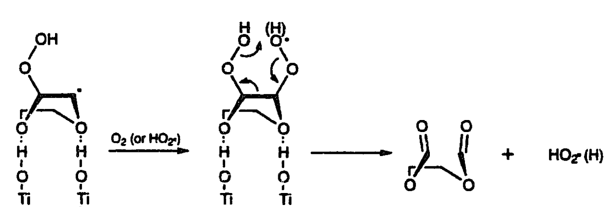
4. Discussion

Ethylene diformate was monitored by absorbance at 200 nm and is considerably more responsive than any saturated compounds lacking carbonyl groups, such as peroxides. However, most products and intermediates in the oxidation of 1,4-dioxane by other agents have been observed by other techniques to be carbonyl compounds [8], and these will respond to 200 nm detection to a degree comparable with ethylene diformate. The dominance of this intermediate during photocatalytic oxidation was confirmed by its isolation, in sufficient quantity for characterization, from a partially degraded solution which originally contained only 800 mg of substrate. It is noteworthy that ethylene diformate is also a major product from reactions with molecular oxygen which occur under other circumstances. For instance, it is the major contaminant arising in storage oxidation, an outcome which can be simulated by photosensitization [9]. It is also the main product when oxidation is initiated by hydroxyl radicals [8]. However, the mechanism proposed for the latter involves several bimolecular reactions of comparatively stable intermediates en route to ethylene diformate, a pathway which fails to accommodate satisfactorily our observation of the apparent primary status of this product in photocatalytic oxidation. Fig. 2 suggests that the first irreversible step in the degradation of ethylene diformate is slower than the whole sequence of events leading to its formation.

The mechanism proposed in Scheme 1 shows the primary events considered plausible for TiO_2-promoted photo-oxidations in general [5], in a sequence which requires two photons for each molecule of ethylene diformate released, but which can take place entirely at a single site. Support for some key steps may be found in observations reported elsewhere. Thus the formation of 1,4-dioxan-2-yl radicals is an outcome of photocatalysis using the semiconductor ZnS [10], and their addition to molecular oxygen is considered necessary to explain the products of hydroxyl-promoted oxidation [8]. Further oxidation of radicals by electron injection into the semiconductor valence band is considered a plausible process [11]. Ring opening of the dioxetane occurs quantitatively when this compound is allowed to reach room temperature from −78 °C [12], and completion of the electrochemical process by the reduction of oxygen, shown separately, is considered an integral part of TiO_2 photo-oxidations [5]. (With ZnS, and in the absence of oxygen, H_2 is generated [10].)



Scheme 1.



Scheme 2.

The alternative pathway shown in Scheme 2 accommodates evidence suggesting that the addition of oxygen or HO_2^- can be faster than electrochemical oxidation [13]. In either case, rapid oxidation continues up to the stage when the adsorption–solution equilibrium shifts significantly towards the solution with the reduced capacity of the ester alkoxyl oxygen to act as an H-bond acceptor.

The apparent absence of the *N,O*-bisformyl derivative of ethanolamine from the products from a similar reaction with morpholine [6] is in sharp contrast with the result with 1,4-dioxane. However, it may be attributable to the additional chemical options available to the secondary amino NH group. For example, morpholine can act as an H-bond donor as well as acceptor, alternative opportunities for bond changes within Scheme 1 can be envisaged and, even if formed, the product may react further, via cyclization for instance.

The adventitious accumulation of formate esters in 1,4-dioxane which is in contact with air reinforces the potential toxic hazard of exposure to samples of the compound [9,14]. An important consideration in all remediation technology is the possibility that harmful intermediates may accumulate in the process [15] and, on both empirical and mechanistic grounds, it is thought that this is least likely to occur in photocatalytic detoxification [13]. The present results may be seen as a cautionary counter-example.

Metabolites of 1,4-dioxane which have been detected, 1,4-dioxane-2-one and *β*-hydroxyethoxyacetic acid, appear to eliminate the intermediacy of formates in the toxicology of the compound [16]. However, a recent study casts some doubt on earlier evidence of the carcinogenicity of pure samples [17]. The possible role of formate esters already present thus appears worthy of some consideration, especially with respect to the inconclusive human epidemiological investigations on the carcinogenicity of 1,4-dioxane [18].

5. Conclusions

1,4-Dioxane is readily mineralized by the combined action of oxygen and UVA/UVB with titanium dioxide as catalyst. Solar radiation would be effective, in principle, and continuing developments in photocatalytic technology promise opportunities for its use to remove this contaminant in due course. However, the photo-oxidation of 1,4-dioxane is an example of the potential in photodetoxification for introducing other toxic contaminants as intermediates. Ethylene diformate is clearly observed as such an intermediate. In addition, its formation as the principal primary product suggests a possible molecular pathway for photocatalysed degradation and that consideration should be given to its possible contribution to the well-known chemical hazard associated with exposure to 1,4-dioxane.

References

[1] J.D. Young, W.H. Braun, L.W. Rampy, M.B. Chenoweth and G.E. Blau, *J. Toxicol. Environ. Health, 3* (1977) 507. L. Fishbein, *Studies in Environmental Science, Vol. 4, Potential Industrial Carcinogens and Mutagens*, Elsevier, New York, 1979, pp. 481–486. I. Lundberg, J. Hogberg, T. Kronevi and B. Holmbert, *Cancer Lett., 36* (1987) 29.

[2] S.C. Rastogi, *Chromatographia, 29* (1990) 441. S. Scalia, M. Guarneri and E. Menegatti, *Analyst, 115* (1990) 929.

[3] R.E. Parales, J.E. Adamus, N. White and H.D. May, *Appl. Environ. Microbiol., 60* (1994) 4527. D. Roy, G. Anagnostu and P. Chaphalkar, *J. Environ. Sci. Health A, 29* (1994) 6.

[4] C.D. Adams, P.A. Scanlon and N.D. Secrist, *Environ. Sci. Technol., 28* (1994) 1812.

[5] M.J. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev., 95* (1995) 69.

[6] S. Doherty, C. Guillard and P. Pichat, *J. Chem. Soc., Faraday Trans., 91* (1995) 1853.

[7] C.G. Carlson, J.E. Hall, Y.Y. Huang, S. Kotila, A. Rauk and D.F. Tavares, *Can. J. Chem., 65* (1987) 2461. J.M.J. Bijen, *J. Mol. Struct., 17* (1973) 69.

[8] C. Nese, M.N. Schuchmann, S. Steenken and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, (1995) 1037.

[9] D. Jewett and J.G. Lawless, *Bull. Environ. Contam. Toxicol., 25* (1980) 118.

[10] S. Yanagida, T. Azuma, Y. Midori, C. Pac and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, (1985) 1487.

[11] H. Gerischer, *Electrochim. Acta, 40* (1995) 1277.

[12] A.P. Schaap, *Tetrahedron Lett., 32* (1971) 1757.

[13] A. Heller, *Acc. Chem. Res., 28* (1995) 503.

[14] N.I. Sax and R.J. Lewis, *Dangerous Properties of Industrial Materials*, Vol. II, van Nostrand-Reinhold, New York, 7th edn., 1989, p. 1626.

[15] W. Klopffer, *Sci. Total Environ., 123* (4) (1992) 145.

[16] Y.T. Woo, M.F. Argus and J.C. Arcos, *Cancer Res., 38* (1978) 1621.

[17] T.L. Goldsworthy, T.M. Monticello, K.T. Morgan, E. Bermudez, D.M. Wilson, R. Jackh and B.E. Butterworth, *Arch. Toxicol., 65* (1991) 1.

[18] NIOSH Criteria for a Recommended Standard. Occupational Exposure to Dioxane, *NIOSH Doc. No. 77-226*, National Institute for Occupational Safety and Health (NIOSH), 1977.