ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 257–262

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

The photodegradation of 2,3-benzofuran and its intermediates, 2-coumaranone and salicylaldehyde, in TiO_2 aqueous suspensions

Laurence Amalric, Chantal Guillard, Pierre Pichat*

URA au CNRS "Photocatalyse, Catalyse et Environnement", Ecole Centrale de Lyon, B.P. 163, 69131 Ecully Cédex, France

Received 4 March 1994; accepted 21 June 1994

Abstract

2,3-Benzofuran (BZF), a mutagenic and carcinogenic compound, was chosen as a model water pollutant to study the TiO_2 photocatalytic degradation of molecules which have two aromatic rings and a built-in oxygen heteroatom. For BZF and its two main degradation intermediates, salicylaldehyde (SA) and 2-coumaranone (2-CO), a relatively good correlation was found between the apparent first-order rate constant of disappearance (approximately 0.059 min^{-1}, 0.0365 min^{-1} and 0.031 min^{-1} respectively) and the measured extent of dark adsorption (about 0.43, 0.134 and 0.108 molecules per square nanometre of TiO_2 respectively) or the logarithm of the 1-octanol–water partition coefficient (2.67_{exp}, 1.75_{exp} and 1.35_{calc} respectively). This illustrates the importance of surface phenomena for these classes of compounds. From the degradation of BZF, 2-CO and SA (studied separately), it was inferred that the larger number of BZF degradation intermediates resulted from the oxidation of the furan ring to produce 2-CO (and perhaps 3-CO), 2,3-dioxobenzofuran and SA, which was further oxidized/hydroxylated to salicylic acid, catechol and dihydroxybenzaldehydes (and perhaps to dioxobenzaldehydes and hydroxyparabenzoquinone or isomers). However, the identification of other compounds with one hydroxyl substituent on the benzene ring and an unopened furan ring demonstrated that the degradation proceeded by a variety of pathways. Although most of these intermediates could be formed by hydroxyl radicals, the involvement of other species cannot be ruled out; in particular, the direct formation of SA from BZF may result from the interaction of superoxide with $BZF^{\cdot +}$. The efficiency of the photocatalytic pollutant degradation was illustrated by the observation that the maximum quantity of each intermediate was less than a few per cent of eliminated BZF.

Keywords: Photodegradation; TiO_2; 2,3-Benzofuran; 2-Coumaranone; Salicylaldehyde

1. Introduction

The photocatalytic treatment of water with TiO_2 has been shown to be efficient for the destruction of many organic micropollutants [1]. However, studies are still required to determine the degradation pathways of typical pollutants which represent various categories of molecular structures. In this respect, detailed analyses of the intermediate products of the photocatalytic degradation of pollutants containing two different aromatic rings and an oxygen heteroatom included in one of the rings have not yet been performed. The present investigation was motivated by this lack of information. 2,3-Benzofuran (BZF) was chosen as the model compound. The photocatalytic destruction of the structurally related, very toxic polychlorodibenzo-*p*-dioxin has been reported [2,3], but the nature of the intermediates was not investigated. In addition, BZF is a mutagenic and carcinogenic compound [4]. It shows acute toxic effects in rabbits when administered orally at a dose of 1 g [5]. Its lethal dose (LD_{50}) is 0.5 g kg^{-1} for mice [5]. It is a constituent of coal tar (0.01%) [5]. Together with indene, it is the raw material used for the production of indene–coumarone resins [5], which are employed in paints, as tackifiers in rubber compounding and as adhesives in the manufacture of flooring tiles [6].

The kinetics of the gas phase reactions of BZF with $OH^{\cdot}$ radicals or O_3 in air at atmospheric pressure and room temperature have been studied [7]. Salicylaldehyde (SA) was observed as a product in both cases. Its formation yield was twice as high in the presence of $OH^{\cdot}$ radicals. The $OH^{\cdot}$ radicals attack both the benzene ring and the 2,3-bond of the furan moiety. In the latter case, which was calculated to account for about 30%

---

*Corresponding author.

1010-6030/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 1010-6030(94)03907-C

of the overall reaction, the resulting radical was progressively transformed into SA by a series of reactions with O_2 and NO.

The reactions of BZF [8], 2,3-dimethylbenzofuran [9] and 3-methylbenzofuran [10] with $^1O_2$ have been investigated. For all compounds, the cleavage of the 2,3-bond was observed, so that the major product of BZF was SA [8]. The mechanism proposed implied the formation of a dioxetane intermediate.

Maissant et al. [11] have studied the potential of ferric complexes to act as catalysts for the oxidation of aromatic compounds by H_2O_2 in acetonitrile. BZF and furan were more rapidly oxidized than other substituted aromatic molecules, such as chlorobenzene. The C=C bond splitting in the furan ring was at the origin of the products. BZF produced SA and (2-hydroxy)phenylacetic acid in a 3:1 ratio via two parallel reactions, since the oxidation of (2-hydroxy)phenylacetic acid did not generate SA.

To sum up, the 2,3-C=C bond in the furan ring is particularly sensitive to oxidation reactions. SA is obtained directly. However, hydroxylation of the benzene ring is also observed.

By the use of high performance liquid chromatography (HPLC) with a diode array detector and gas chromatography/mass spectrometry (GC/MS) analysis, we have attempted to identify some aromatic intermediates of BZF degradation in UV-irradiated TiO_2 aqueous suspensions. Control experiments of the degradation of the two principal aromatic intermediates, 2-coumaranone (2-CO) and SA, were carried out under the same conditions to obtain a better understanding of the BZF degradation pathways. The kinetics of disappearance of BZF, 2-CO and SA, as well as of the appearance/disappearance of some of their aromatic intermediate products, were studied to assess the persistence of these aromatic pollutants. It has previously been shown that the logarithm of the 1-octanol–water partition coefficient (K_{ow}) is one of the two characteristics which together can be used to evaluate the rate of photocatalytic disappearance of chlorophenols [12,13]. Hence, we have correlated, for the present compounds, the rates of disappearance with the values of log K_{ow} and the extent of adsorption of each pollutant on the photocatalyst.

2. Experimental details

2.1. Materials

BZF (99.5%), SA (98%) and 2-CO (97%) were obtained from Aldrich, and were used as received. The intermediate products of their degradation were also obtained from Aldrich, except 3-coumaranone (Lancaster). Methanol (Rathburn HPLC grade), acetonitrile (Scharlau), orthophosphoric acid (85%; Merck) and hydrochloric acid (purity, 99.999%; 37%; Merck) were employed either as eluents or to modify the pH. The photocatalyst was TiO_2 Degussa P-25 (mainly anatase, non-porous 50 m^2 g^{-1}).

2.2. Reactors and light sources

The batch photoreactor was a cylindrical flask (100 ml), with a bottom optical window of about 4 cm in diameter, and was open to air. Irradiation was provided by a high-pressure mercury lamp (Philips HPK, 125W) which was filtered by a circulating water cell (thickness, 2.2 cm) equipped with a 340 nm cut-off filter (Corning 0.52). The radiant flux, measured with a power meter (UDT, model 21A), entering the photoreactor was 52 ± 2 mW cm^{-2}. The corresponding number of photons per second potentially absorbable by TiO_2 was $(1.87 \pm 0.07) \times 10^{17}$.

2.3. Initial conditions

In the case of HPLC, the initial concentration was 20 mg l^{-1} for each compound, i.e. 0.17 mmol l^{-1} for BZF, 0.16 mmol l^{-1} for SA and 0.15 mmol l^{-1} for 2-CO; under these conditions the initial pH was about 5.2. The solution (20 ml) introduced into the photoreactor was magnetically stirred with TiO_2 (2.5 g l^{-1}) in the dark for 60 min before irradiation, in order to reach equilibrated adsorption. In the case of the experiments intended to identify the degradation intermediates, the initial concentrations were 2.38 mmol l^{-1} (BZF), 4.86 mmol l^{-1} (SA) and 0.53 mmol l^{-1} (2-CO) and the suspensions were UV irradiated for 1.5 h or 3.5 h.

2.4. Analyses

Millipore discs (0.45 μm) were used to remove particulate matter before HPLC analysis. The HPLC system comprised an LDC/Milton Roy Constametric 3000 isocratic pump and a Spectro Monitor UV detector adjusted at 240 nm or a photodiode array (Varian Polychrom 9065 with Varian LC Star System and a Compaq 286-A microcomputer). A reverse-phase column (length, 25 cm; inner diameter, 4.6 mm) packed with Spherisorb 5 ODS 2 was used. The mobile phase was composed of methanol (60%) and deionized doubly distilled water (40%) into which orthophosphoric acid (0.75%, v/v) was added.

GC analyses were performed with an HP 5890 chromatograph coupled to an HP 5971 mass detector (chemical ionization (CI) and electron ionization (EI)) and an HP 386 microcomputer. The capillary column (length, 25 m; inner diameter, 0.32 mm) was packed with CPSil 5CB (thickness, 1.2 μm). The injection was made in the splitless mode. The temperature of the column was raised from 308 to 323 K (20 K min^{-1}), and then to 523 K (5 K min^{-1}); this latter temperature was maintained for 5 min. The filtered water samples were acidified to pH 1 with HCl; the organic compounds were extracted with acetonitrile and the solvent was eliminated in a rotary evaporator at room temperature.

3. Results and discussion

3.1. Photocatalytic degradation of BZF

3.1.1. BZF adsorption and kinetics of BZF disappearance

BZF is very poorly soluble; its 1-octanol–water partition coefficient, K_{ow}, is 2.67 [14]. Accordingly, a relatively high percentage of the BZF molecules can be expected to leave the bulk of water and to cover the TiO_2 surface. Indeed, the percentage of adsorbed BZF molecules in the dark was 53%±3% or 0.43±0.02 molecules per square nanometre of TiO_2 for the initial concentration of 0.17 mmol l^{-1}. As the surface area of the benzene molecule is 0.4 nm^2 [15], we suggest that the BZF molecule surface area is about 0.7 nm^2. Therefore about one-third of the TiO_2 surface was covered by adsorbed BZF molecules.

The kinetics of disappearance of BZF corresponded to an apparent first-order law, and the corresponding rate constant, k_{app}, was approximately 5.9×10^{-2} min^{-1} at pH 5.2. Under the same conditions, except for a slight difference in pH, BZF was eliminated more rapidly than 1,2-dimethoxylbenzene (1,2-DMB) ($k_{\text{app}}\approx5\times10^{-2}$ min^{-1}; pH 5.8) [16], despite the presence of two electron-donating substituents in the latter compound. However, small traces of BZF (about 0.17 μmol l^{-1}, i.e. about 0.1% of the initial concentration) were still detected by HPLC after the suspension had been UV irradiated for 2.5 h.

The disappearance of BZF by direct photolysis was relatively important, at least within the first 2 h of irradiation, but its rate was markedly lower than that observed in the presence of TiO_2 (Fig. 1). Although BZF exhibited a residual absorption in the wavelength range used ($\lambda>340$ nm), direct photolysis could be neglected under photocatalytic conditions, because TiO_2 behaved as an internal filter.

3.1.2. Intermediate products of photocatalytic BZF degradation

The high performance liquid chromatogram (detection at $\lambda=240$ nm) contained nine peaks corresponding to the degradation products of BZF. By comparing the retention time and the UV spectrum associated with each peak with those of authentic compounds, SA, 2-CO and catechol (CT) were identified.

The use of GC/MS corroborated the formation of these intermediates (SA: $t_r=12.8$ min; CT: $t_r=16.3$ min; 2-CO: $t_r=18.6$ min). It also allowed the identification of 3-coumaranone ($t_r=18$ min), 2,5-dihydroxyphenylacetic γ-lactone ($t_r=27.9$ min; 2,5-DHPAL or 5-hydroxy-2-coumaranone), 2,4- and 2,5-dihydroxybenzaldehyde ($t_r=24.7$ and 23.3 min; DHBA) by comparison of the observed mass spectra with those of the authentic compounds (Scheme 1). The formation of coumaranones was not observed when the oxidation of BZF was realized with O_3 or OH$^\bullet$ radicals in atmospheric air [7], with $^1O_2$ in non-aqueous solvents [17] or with H_2O_2 [11]. This difference can be attributed to (a) the existence of active species other than OH$^\bullet$ radicals in photocatalysis, (b) the slower degradation of coumaranones by photocatalysis than by the other processes, or (c) the role of the TiO_2 surface in stabilizing the enol resulting from OH substitution at positions 2 or 3 by the formation of a ketone tautomer.

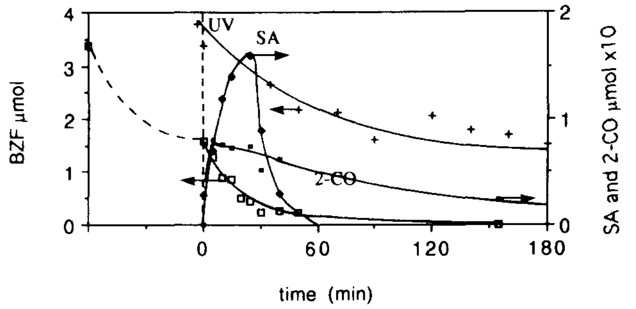


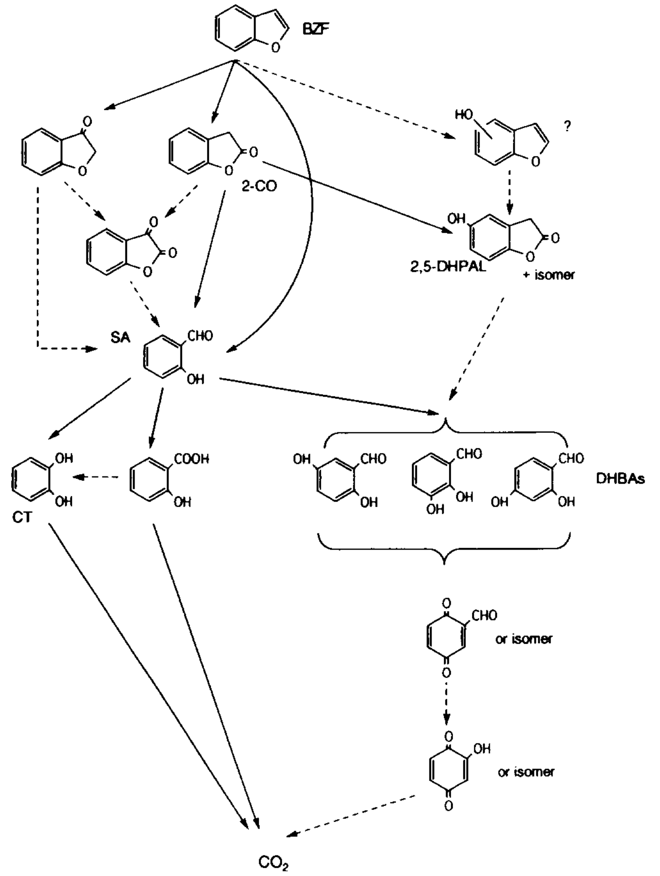
Fig. 1. Kinetics of the disappearance of BZF in UV-irradiated TiO_2 suspensions (open squares) and of the resulting appearance/disappearance of 2-CO and SA. The curve indicated by + shows the disappearance of BZF under UV irradiation in the absence of TiO_2. Note that the ordinate scale is enhanced 20 times for the curves relating to 2-CO and SA.

The formation of some other cyclic intermediates is also proposed on the basis of the interpretation of the mass spectra (CI and EI) as detailed below.

The mass spectrum of the compound eluted at $t_r=20.3$ min was very similar to that of 2,3-dioxobenzofuran included in the NBS library of the microcomputer to which the mass spectrometer was connected. Therefore the formation of this intermediate is probable.

The molecular mass, 124, of the intermediate compound eluted at 12.1 min was inferred from the CI mass spectrum ($M+1=125$). The presence of two C=O groups and one COH group could account for the difference in mass between the EI molecular peak and the EI base peak at $m/e=39$ ($39=124-(2\times28+29)$), which was supported by the pairs of peaks of mass units 96 and 95 (124−28 or 29) and 68 and 67 (95−28 or 29). The base peak was attributed to the moiety –CH=CH=CH. Therefore the compound could be one of the trioxocyclohexene isomers or a corresponding enol tautomer, i.e. a hydroxybenzoquinone whose most stable isomer is hydroxyparabenzoquinone.

Three chromatographic peaks ($t_r=19.1$, 21.2 and 21.3 min) corresponded to very similar mass spectra (except



Scheme 1. Scheme showing the various intermediate products of the photocatalytic degradation of BZF, 2-CO and SA and the suggested pathways. Salicylic acid, 2-CO, CT, DHBAs and 2,5-DHPAL were identified by comparison of their mass spectra with those of the authentic compounds. The formation of 2,3-dioxobenzofuran was deduced from a comparison of its mass spectrum with a mass spectrum reported in the literature. The tentatively proposed formulae of the other intermediates resulted from the interpretation of the mass spectra.

that the relative intensity of the fragment at $m/e = 121$ was high only for the peak with a retention time of 21.2 min). Therefore the corresponding compounds were probably isomers. The CI mass spectrum for the peak at $t_r = 19.1$ min indicated that the molecular mass was 134 ($M+1 = 135$). From the strong intensity of the EI molecular peak, it was inferred that the compound was aromatic. The mass loss of 29 ($M-29=105$) suggested the elimination of a COH moiety. On this basis, it was tempting to attribute these mass spectra to hydroxy-2,3-benzofuran isomers with the OH group on the six-membered ring. However, as we cannot suggest which fragment of these compounds would account for the mass peak at $m/e = 78$, this assignment is uncertain.

Finally, the intermediate compound which eluted at $t_r = 6.7$ min was unidentified. Although its retention time was similar to those of 2-(3-H)-furanone and 2,4-dioxocyclopentene, its mass spectrum was not in agreement.

3.1.3. *Kinetics of the formation/destruction of the intermediate products*

Owing to the calibration of their HPLC peaks, 2-CO and SA were quantified in terms of degraded BZF; the maximum values were about 3.8% reached within 5 min and about 5.5% obtained within 25 min (Fig. 1). The maximum 2-CO concentration was attained much earlier than that of SA; this could indicate that 2-CO is degraded into SA. However, since SA appeared during the first minutes of irradiation (Fig. 1), it must also be produced from BZF without the intermediate formation of 2-CO, as has been shown in the case of other oxidation methods [7,11,17].

To verify whether or not SA could be generated by the photocatalytic degradation of 2-CO, and in an attempt to reveal the existence of other intermediates of BZF degradation, 2-CO and SA were degraded separately over UV-irradiated TiO_2 under the same conditions.

3.2. *Photocatalytic degradation of 2-CO*

3.2.1. *2-CO adsorption and kinetics of 2-CO disappearance*

The amount of 2-CO adsorbed in the dark was less important than that of BZF: $15\% \pm 1\%$, i.e. 0.108 ± 0.007 molecules per square nanometre of TiO_2 (instead of 0.43 for BZF) for an equivalent initial concentration. This difference was consistent with the calculated value [18] of $\log K_{ow} = 1.35$, compared with 2.67 for BZF.

2-CO disappeared by photocatalytic treatment with an apparent first-order kinetic constant, k_{app}, of 3.1×10^{-2} min^{-1}. Traces of 2-CO (about 1 $\mu mol\ l^{-1}$; 0.7% of the initial concentration) were still present after 2 h of irradiation. For these two structurally related molecules, BZF and 2-CO, the order in k_{app} is consistent with the order in the extent of adsorption, as in the case of dimethoxybenzenes [19].

3.2.2. *Intermediate products: kinetics of formation/disappearance of SA*

The high performance liquid chromatogram obtained by analysing the 2-CO suspension after irradiation in the presence of TiO_2 contained less peaks than that recorded in the case of BZF degradation. SA was identified by its UV spectrum and its formation was confirmed by GC/MS analysis ($t_r = 12.8$ min). CT ($t_r = 16.3$ min), 2,5-DHBA ($t_r = 23.3$ min) and 2,5-DHPAL ($t_r = 27.9$ min) were identified by comparing the mass spectra recorded with those of the authentic compounds. The EI mass spectrum of another intermediate, eluted at 24.2 min, contained the same fragments as that of 2,5-DHPAL with, however, some differences in the relative intensities. Therefore it was attributed to a 2,5-DHPAL isomer. For the compound eluted at 22.5 min, the mass spectrum indicated that it was an aromatic, with a molecular mass of 166, containing two C=O or COH groups (mass losses of 28 and 29). However, any of the molecular structures derived from 2-CO by simple mechanisms did not readily account for the intense fragment at $m/e = M - 32$.

The formation of SA was quantified by HPLC. Its maximum value represented about 1.2% of degraded 2-CO after 15 min of irradiation (Fig. 2).

3.3. Photocatalytic degradation of SA

3.3.1. SA adsorption and kinetics of SA disappearance

The percentage of adsorbed SA was 17.0 ± 0.5, i.e. 0.134 ± 0.004 molecules per square nanometre of TiO_2 for an initial concentration of 0.16 $mmol^{-1}$, while the measured value of $\log K_{ow}$ for SA is 1.70 or 1.81 [14].

The extent of adsorption on TiO_2 can be correlated with $\log K_{ow}$ for BZF, 2-CO and SA. In addition, if 1,3- and 1,4-DMB, for which we have measured the adsorption under similar conditions [19], are included, the correlation coefficient is 0.96. However, the values of 1,2-DMB do not fit into this correlation, possibly because the two bulky methoxy groups in ortho positions hinder the approach of this compound towards the surface of TiO_2. Similarly, a good correlation has been obtained for several para- and meta-monosubstituted anisoles [20].

SA had completely disappeared within 80 min of UV irradiation (Fig. 3). The corresponding apparent first-order kinetic constant, k_{app}, was 3.65×10^{-2} min^{-1}. The values of k_{app} for BZF, 2-CO and SA were relatively well correlated with the extent of adsorption ($r = 0.993$) and $\log K_{ow}$ ($r = 0.993$). These correlations point to the importance of surface phenomena for these types of compound, even if we keep in mind that only three pollutants were considered. Obviously, other factors intervene, such as the electron availability on the aromatic rings [12,13,20] or the reactivity, since higher rates are observed for poorly adsorbing phenols or alcohols than for well-adsorbing substituted benzoic acids [21].

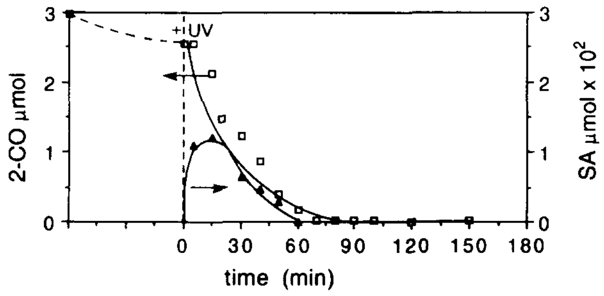


Fig. 2. Kinetics of the disappearance of 2-coumaranone in UV-irradiated TiO_2 suspensions and of the resulting appearance/disappearance of salicylaldehyde. Note that the ordinate scale is enhanced 100 times in the second case.

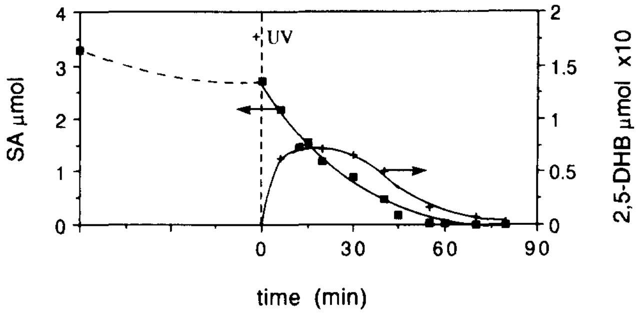


Fig. 3. Kinetics of the disappearance of salicylaldehyde in UV-irradiated suspensions and of the resulting appearance/disappearance of 2,5-dihydroxybenzaldehyde. Note that the ordinate scale is enhanced 20 times in the second case.

3.3.2. Intermediate products of photocatalytic SA degradation

Seven intermediates have been detected by HPLC. However, only 2,5-DHBA has been identified by this technique. Using GC/MS, the formation of 2,5-DHBA ($t_r = 23.3$ min) was confirmed, and 2,3-DHBA ($t_r = 16.7$ min), CT ($t_r = 16.3$ min) and salicylic acid ($t_r = 21$ min) were identified. The formation of salicylic acid was expected given the oxidative properties of the photocatalytic process. According to Hollemann's rules, 2,5-DHBA and 2,3-DHBA should indeed be produced preferentially among the DHBA isomers because of the meta orientation induced by the CHO group and the ortho or para orientations caused by the OH group. Similarly, it has been shown that the quantities of 2,3- and 2,5-DHBA are more important than those of 2,4- and 2,6-DHBA when salicylic acid is degraded by electrochemically produced $OH^{\cdot}$ [22]. However, it should be noted that 2,4-DHBA was detected when BZF was photocatalytically degraded; therefore it may be produced by another route.

From the interpretation of the mass spectrum of the compound eluted at 15.9 min, dioxobenzaldehyde was identified. The CI mass spectrum indicated that the molecular mass was 136 ($M + 1 = 137$). The high intensity of the molecular peak indicated an aromatic structure. The presence of an aldehyde functionality was inferred from the fragment 107 which could correspond to the loss of HCO from $m/e = 136$ and CO from $m/e = 135$. The further losses of 28 mass units were consistent with the presence of two carbonyl groups: fragments at $m/e = 79$ (107 − 28) and $m/e = 51$ (79 − 28). This latter ion was assumed to be C_4H_3.

2,5-DHBA formation/disappearance was quantified by HPLC (Fig. 3); the maximum concentration corresponded to about 3.7% of degraded SA within 20 min of irradiation.

3.4. Suggested degradation pathways of BZF

Scheme 1 presents all the aromatic intermediates of the photocatalytic degradation of BZF which have been identified in this study. As in the case of other oxidation methods, SA occupies a central place among the intermediates. Our results show that it is formed via 2-CO (and perhaps 3-CO and/or 2,3-dioxobenzofuran). Coumaranones could result from the substitution of a hydrogen atom by a hydroxyl group on the furan ring; the enols thus formed would be stabilized into the corresponding ketones, possibly owing to the TiO_2 surface. Comparison of the kinetics of formation of 2-CO and SA from BZF (Fig. 1) also suggests that SA could be generated by another pathway. It could be produced by the attack of $OH^{\bullet}$ radicals, followed by a reaction with dioxygen, as shown [7] for the oxidation of BZF by these entities under tropospheric conditions. It may also be produced by the reaction between superoxide and the $BZF^{\bullet +}$ radical cation, i.e. via a mechanism involving the formation of an endoperoxide and the subsequent cleavage of the 2,3-bond. A similar mechanism was relatively suggested for the photocatalytic oxidation of 1,2-DMB [16].

Subsequently, SA could be hydroxylated to DHBAs or oxidized to salicylic acid. The formation of CT from either SA or salicylic acid is consistent with the hydroxylation of aromatics often shown to occur in the photocatalytic process [1]. The coexistence of DHBAs and dioxobenzaldehydes is also in line with similar coexistences found during photocatalytic degradations, such as those of *p*-benzoquinone and hydroquinone when the starting pollutant is phenol [23] or 4-chlorophenol [24]. Further studies are needed to determine the origin of these quinone compounds. They could be formed by the interaction of phenoxyl radicals with superoxide whose importance as a reactant has been suggested recently [16]. On the other hand, the reduction of quinones to the corresponding dihydroxybenzene compounds might be envisaged, since reduction steps involving the organic molecules and dioxygen have been observed in photocatalytic water treatment [25].

Finally, the existence of 2,5-DHPAL (and presumably its isomers) and other two-ring compounds hydroxylated on the benzene ring (Scheme 1) is not unexpected, since the photocatalytic hydroxylation of monocyclic aromatics is a well-known mechanism [1]. These compounds can easily be transformed into DHBAs. Their existence indicates the simultaneous hydroxylation/oxidation of both nuclei in BZF and illustrates the occurrence of multiple degradation pathways. However, it should be kept in mind that the concentrations of the intermediates sufficient to be quantified were much smaller than the BZF initial concentration (Figs. 1–3). Finally, the nature of the intermediates and, in particular, those whose concentration is measurable confirms the greater stability of the six-membered ring, compared with the furan moiety, towards photocatalytic oxidation. This was also found for other oxidation methods [8,11].

Acknowledgement

Financial support from the Commission of European Communities (contract STEP-CT 90-0106-C), in the form of a scholarship to L.A., is gratefully acknowledged.

References

[1] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat and N. Serpone, in R.G. Helz, R.G. Zepp and D.G. Crosby (eds.), *Aquatic and Surface Chemistry*, Lewis Publishers, Boca Raton, 1994, Chapter 21, pp. 261–316.

[2] M. Barbeni, E. Pramauro, E. Pelizzetti, N. Serpone and M.A. Jamieson, *Chemosphere, 15* (1986) 1913.

[3] E. Pelizzetti, M. Borgarello, C. Minero, E. Pramauro, E. Borgarello and N. Serpone, *Chemosphere, 17* (1988) 499.

[4] National Toxicology Program Technical Report Series, *NTP-TR-370*, 1989.

[5] B. Elvers, S. Hawkins, M. Ravenscroft, J.F. Rounsaville and G. Schulz (eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A12, VCH, 5th edn., 1990, pp. 130–132.

[6] D. McNeil in *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 22, Wiley, New York, 3rd edn., 1978, pp. 564–600.

[7] R. Atkinson, J. Arey, E.C. Tuazon and S.M. Aschmann, *Int. J. Chem. Kinet., 24* (1992) 345.

[8] D.R. Berdahl and H.H. Waserman, *Isr. J. Chem., 23* (1983) 409.

[9] G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, (1971) 1705.

[10] J.M. Fernandez, *Ph.D. Thesis*, Yale University, 1968.

[11] J.M. Maissant, J.M. Bodroux, C. Bouchoule and M. Blanchard, *J. Mol. Catal., 9* (1990) 237.

[12] P. Pichat, C. Guillard, C. Maillard, L. Amalric and J.-C. D'Oliveira, in D.F. Ollis and H. Al-Ekabi (eds.), *Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, pp. 207–223.*

[13] J.-C. D'Oliveira, C. Minero, E. Pelizzetti and P. Pichat, *J. Photochem. Photobiol. A: Chem., 72* (1993) 261.

[14] A. Leo, C. Hansch and D. Elkins, *Chem. Rev., 71* (1971) 525.

[15] S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1967, p. 80.

[16] L. Amalric, C. Guillard and P. Pichat, *Res. Chem. Intermed., 20* (1994) 579.

[17] H.H. Wasserman and D.R. Berdahl, *Photochem. Photobiol., 35* (1982) 565.

[18] W.J. Lyman, in W.J. Lyman, W.F. Reehl and D.H. Rosenblatt (eds.), *Handbook of Chemical Property Estimation Methods*, American Chemical Society, 1990, pp. 1.1–1.54.

[19] L. Amalric, C. Guillard, N. Serpone and P. Pichat, *J. Environ. Sci. Health, A28* (1993) 1393.

[20] L. Amalric, C. Guillard, E. Blanc-Brude and P. Pichat, unpublished results, 1900.

[21] J. Cunningham, G. Al-Sayyed and S. Srijaranai, in G.R. Helz, R.G. Zepp and D.G. Crosby (eds.), *Aquatic and Surface Chemistry*, Lewis Publishers, Boca Raton, 1994, Chapter 22, pp. 317–348.

[22] M.A. Oturan, J. Pinson, J. Bizot, D. Deprez and B. Terlain, *J. Electroanal. Chem., 334* (1992) 103.

[23] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka and A. Itaya, *Bull. Chem. Soc. Jpn., 58* (1985) 2015.

[24] G. Al-Sayyed, J.-C. D'Oliveira and P. Pichat, *J. Photochem. Photobiol. A: Chem., 58* (1991) 99.

[25] C. Maillard-Dupuy, C. Guillard and P. Pichat, in press.