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Catalysis Today 29 (1996) 309–315

CATALYSIS TODAY

Kinetic studies of depollution process in TiO_2 Slurries: interdependences of adsorption and UV-intensity

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Abstract

Monochlorophenols (CP) and hydroxybenzoic acids (HBA) have been used to model poorly-adsorbing and strongly-adsorbing pollutants in aqueous slurries containing TiO_2(P25). Profiles are presented and compared for the manner in which initial rates for TiO_2-photocatalysed depletions of those pollutants under low, moderate and high fluxs of 365 nm photons varied as a function of various initial aqueous-phase concentrations attained after adsorption–desorption equilibration in the dark. Marked intensity-related differences are, thus, observed, especially for well-adsorbing 3-chloro 4-hydroxy benzoic acid (CHBA). Differences stem in part from a major rate-determining role for primary photooxidation events in the surface solution monolayer under low intensity, whereas under high intensity that role is filled by desorption of strongly adsorbed products and/or by activated diffusion along surfaces within TiO_2 aggregates which is altered under high photon flux.

Keywords: TiO_2 depollution

1. Introduction

Previously reported experimental differences between 'dark' adsorption isotherms for poorly-adsorbing chlorophenols, and well-adsorbing hydroxybenzoic acids (HBA) [1–4] may be rationalised as per the diagrammatic inserts on top of Fig. 1; that above Fig. 1A envisages strong HBA adsorption in terms of chemisorption requiring displacement of a basic singly coordinated OH group from the hydrated surface monolayer on TiO_2, whereas that above Fig. 1B envisages the weaker CP adsorption in terms of physical adsorption on top of the outer layer of such OH groups. Comparisons are made in the present work between the manners in which kinetics and efficiency of TiO_2-sensitized photocatalytic depletion of the poorly-adsorbing CP's and the strongly-adsorbing HBA's are affected by such differences in adsorption and by changes in the flux of 365 ± 10 nm photons incident on the aerated stirred aqueous slurries. All such slurries were allowed to come into adsorption–desorption equilibrium before commencing UV-illumination.

2. Experimental

Details have been given elsewhere of procedures and equipment used to determine, with the aid of HPLC analysis, the decreases in aqueous phase concentrations of CP's and HBA's caused *firstly* by adsorption onto TiO_2

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SSDI 0920-5861(95)00297-9

upon equilibration for 0.5 h in the absence of UV-illumination and *subsequently* during illumination of 30 ml aliquots of dark preequilibrated slurry (containing 60 mg of TiO_2 P25) by nominally 'low', 'moderate' or 'high' fluxs of photons of 365 ± 10 nm (respectively 1.7×10^{16} min^{-1}, 5.6×10^{17} min^{-1} and 2×10^{18} min^{-1} — as evaluated with a chemical-actinometer solution in the photoreactor) [1–4]. Initial rates of TiO_2 photocatalysed depletions (PCD) of organic micropollutant from the aqueous phase during such UV-illumination — denoted respectively by $R^*_{\mathrm{i.L.}}$, $R^*_{\mathrm{i.m.}}$ or $R^*_{\mathrm{i.h.}}$ — were determined from the slopes of linear plots of aqueous phase concentration vs. duration of illumination, e.g., $R^*_{\mathrm{i.L.}}$ (CHBA) signifies initial rate for photodepletion of 3-chloro 4-hydroxybenzoic acid under low photon flux, whilst $R^*_{\mathrm{i.h.}}$ (4-CP) denotes that for 4-chlorophenol under high photon flux. By virtue of the moderately high TiO_2 loading ($\equiv 2$ g dm^{-3}) and the upward entry of UV-illumination into the photoreactor within which the TiO_2 particles of the aqueous aerated slurries were subject to vigorous magnetic stirring, the photon-flux experienced by individual TiO_2 particles (and any species adsorbed thereon) ranged from the nominal values denoted as 'low', 'moderate' or 'high' (when particles were within ca. 0.1 mm of the photoreactor bottom) to very much lower values upon recirculation away from the bottom of the slurry. In view of the resultant fluctuating nature of the photon-flux experienced by individual particles within the stirred slurry, meaningful tests for dependence of initial rates upon intensity such as reported changes from dependence upon $I^{1/2}$ at high photon flux to first-order dependence at low flux, [5,6], are not available from present data.

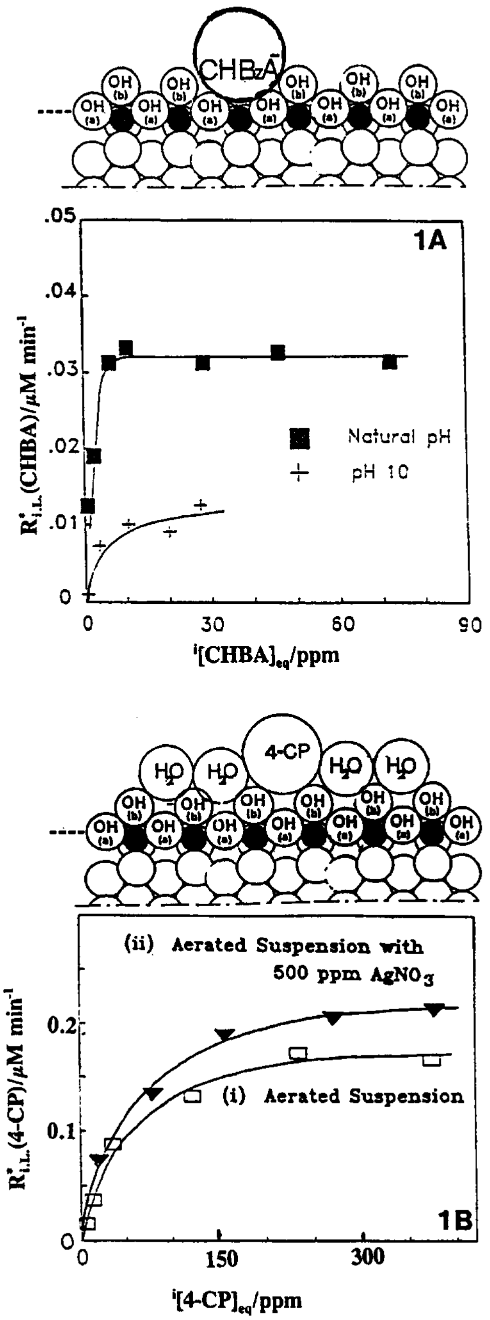

Fig. 1. Contrasting profiles for the variation in initial $R^*_{\mathrm{i.L.}}$ with initial pre-equilibrated C_{eq} under low flux for TiO_2-photocatalysed depletions at 295 K of $[CHBA]_{aq}$ (plots in Fig. 1A), or of 4-CP (plots in Fig. 1B). Profiles obtained for aerated slurries at natural pH unless otherwise indicated. The insert above each part schematically represents the likely type of adsorption of the relevant chlorinated solute at that solution/TiO_2 microinterface. Symbols $OH_{(a)}$ and $OH_{(b)}$ respectively denote 'acidic' or 'basic' hydroxyls.

3. Results and discussion

3.1. Low Intensity Initial PCD Rates, $R^*_{i.L.}$

Plots A and B of Fig. 1 summarise $R^*_{\mathrm{i.L.}}$ values measured when previously dark-equilibrated $TiO_2/(CHBA)_{aq}$ or $TiO_2/(4\text{-}CP)_{aq}$ slurries were exposed to the lowest near-UV intensity used in this study. Despite its obvious disadvantage in producing low, difficult-to-measure values of $R^*_{i.L.}$, data at this low intensity were of particular interest because of least likelihood for serious illumination-induced perturbation of whatever adsorption–desorption equilibrium had previously been established with the surface solution monolayer (ssm) in the dark. Added interest stemmed from the attainment on these conditions of the highest values of relative efficiency for photodepletions at natural pH, viz. ${}^{r}\Phi'_{CHBA} = 1.54 \times 10^{-2}$ and ${}^{r}\Phi'_{4\text{-}CP} = 1.63 \times 10^{-1}$. Data for $R^*_{i.L.}$ (CHBA) on the upper plot in Fig. 1A were obtained with suspensions having their natural pH of ca. 3.9–5.6; those on the lower plot with suspensions having their pH adjusted to 10 by appropriate addition of KOH. The contrast between plots (i) and (ii) demonstrates a strong inhibiting effect of high pH upon $R^*_{i.L.}$ which resembled a qualitatively similar inhibiting effect of pH ca. 10 noted previously upon dark-adsorption isotherms for uptake of CHBA into the ssm at $TiO_2/(CHBA)_{aq}$ microinterfaces [2]. Since pH ca. 10 is much greater than the point of zero charge of TiO_2 (pzc = ca. 5.8) or pK of CHBA (ca. 3), repulsive interaction between $(CHBA^-)_{aq}$ and TiO_2 particles carrying net negative charge was one factor considered to contribute to the lower extent of equilibrium adsorption observed previously at the higher pH. The chemisorption model above Fig. 1A implies that another factor would be greater competition by hydroxide ions for chemisorption sites within the ssm at pH ca. 10. The new profiles now presented within Fig. 1A for initial $R^*_{i.L.}$ (CHBA) vs. initial $[CHBA]_{eq}$ likewise demonstrate a variation with pH. Such similarity of response to pH change could be understood on the basis that the primary rate-determining process (rdp) for R^* (CHBA) was reaction of CHBA species — chemisorbed in the ssm to pH-dependent extent — with highly oxidising species (h^+ and/or OH) generated by TiO_2^* at those microinterfaces. Even the highest value for $R_{i.L.}$ (CHBA) in Fig. 1A corresponds, however, to a relative efficiency ${}^{r}\Phi_{CHBA}$ of just 0.015, thereby implying that such primary photoxidation processes experienced substantial competition from recombination of h^+ and/or OH with electrons even at this lowest intensity.

If primary photooxidation events within the ssm had likewise represented the main rdp contributing to ${}^{r}\Phi_{4\text{-}CP}$ under low intensity, it was to be expected that $R^*_{i.L.}$ (4-CP) would firstly, be lower and, secondly, follow a different profile with $[4\text{-}CP]_{eq}$ than that for CHBA in Fig. 1A. The first expectation was based on observations that for concentrations ≤ 100 ppm any 4-CP chemisorption was an order-of-magnitude lower than for CHBA [2], whereas comparison of plots in Fig. 1B with those in Fig. 1A show instead a much higher $R^*_{i.L.}$ for 4-CP. This indicates a need to take into account additional mechanistic contributions to $R^*_{i.L.}$ (4-CP). Contributions by photooxidation events outside the TiO_2 ssm seem to be implied by the 80% increase in $R^*_{i.L.}$ (4-CP) observed over the $[4\text{-}CP]_{eq}$-range 100 → 250 ppm, since evidence was previously found for increases in multilayer-type adsorption in that range [4]. Another point of interest is the relatively small difference between plots in Fig. 1B. This may be interpreted as supporting a rate-determining role for reaction events involving oxidising species photocatalytically generated by TiO_2^* (but not necessarily confined to the ssm) and disfavouring such a role for electron-trapping at the TiO_2^* surfaces by O_2 adsorbed from the aerated aqueous phase. Data on the upper plot were measured upon dark preequilibrated slurries containing 400 ppm of $AgNO_3$ in addition to the indicated initial $[4\text{-}CP]_{eq}$ values. The resulting enhancement by Ag^+ in availability of electron-trapping species at the microinterfaces would only be expected to cause a large increase in $R^*_{i.L.}$ (4-CP) if, in its absence, trapping of electrons had represented the dominant rdp for data on the lower plot. An increase of only ca. 25% in $R^*_{i.L.}$ (4-CP), as observed in Fig. 1B, thus, argues against a substantial efficiency-

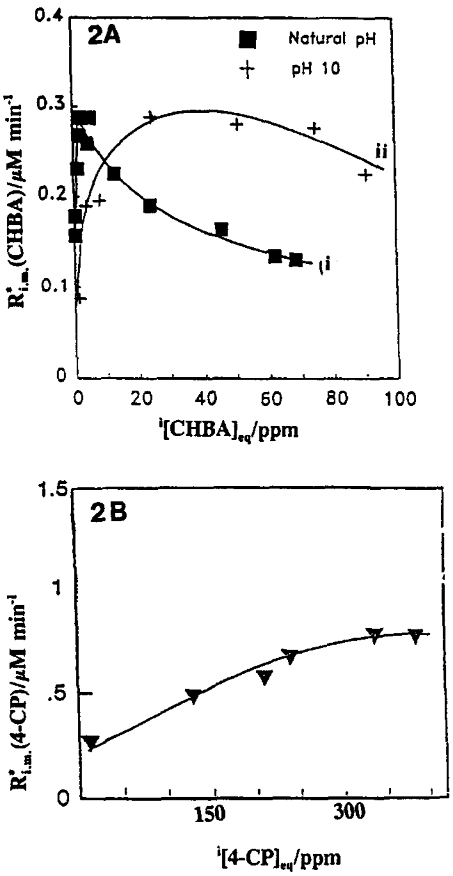

Fig. 2. Contrasting profiles as per legend to Fig. 1, but under moderate flux, i.e., for $R^*_{\mathrm{i.m.}}$ (CHBA) in Fig. 2A and $R^*_{\mathrm{i.m.}}$ (4-CP) in Fig. 2B. The two plots within 2A illustrate a notably different profile at pH 10, plot (ii), from that at natural pH, plot (i).

limiting role for electron-trapping in the absence of Ag^+. In view of the low intensity used and observations upon *initial* rates only, interference/complications from deposition of metallic silver were avoided.

3.2. 'Moderate-Intensity' initial rates $R^*_{i.m.}$

Fig. 2A summarises values obtained for $R^*_{\mathrm{i.m.}}$ (CHBA) upon exposure to an intermediate flux of 5.6×10^{17} photons min^{-1}. Interesting features of plot (i) in Fig. 2A include an initial precipitous rise in $R^*_{\mathrm{i.m.}}$ to a plateau at $C_{\mathrm{eq}} = 4$–13 ppm, and a subsequent gradual 50% decline from that plateau whilst C_{eq} increased from 13 to 75 ppm. Those observations could be rationalised by an hypothesis that, during the 30–60 min illumination time required for measurement of R^*_{i} (CHBA), no significant inhibiting effect could become significant until an empirical (extent-of-adsorption × net-flux) parameter exceeded a critical value (here manifested for CHBA in natural pH conditions when $C_{\mathrm{eq}} > 13$ ppm and net flux in 30 min exceeded ca. 3×10^{19} photons). Inclusion of an extent-of-adsorption factor in this empirical parameter also provides a basis for rationalizing two other observations illustrated in Fig. 2: (i) that a pH of 10, which is known to decrease adsorption, delayed onset of the negative order dependence of $R^*_{\mathrm{i.m.}}$ (CHBA) to higher C_{eq} and (ii) that no negative-order of $R^*_{\mathrm{i.m.}}$ (4-CP) was observed for poorly adsorbing 4-CP (cf. Fig. 2B).

3.3. 'High-Intensity' initial PCD rates, $R^*_{i.h.}$

Fig. 3A summarises initial PCD rates, $R^*_{\mathrm{i.h.}}$ (CHBA), measured under 'high' flux of 365 nm photons for suspensions containing the various dark-preequilibrated concentrations of CHBA indicated along the bottom axis. Different symbols are employed on the figure to distinguish between single-reactant $R^*_{\mathrm{i.h.}}$ values measured at natural pH, or at pH ca. 10, from those obtained at natural pH in the presence of added Ag^+. Three features strikingly different from the data obtained for the same system under low intensity (cf. Fig. 1A) are evident for the ${}^{\mathrm{i}}C_{\mathrm{eq}}$ dependence of $R^*_{\mathrm{i.h.}}$ (CHBA) of data in Fig. 3A: firstly, a negative-order dependence in the C_{eq} range 10–80 ppm; secondly, an apparently zero-order dependence in the range from 80 to 200 ppm, indicative of a low ${}^{\mathrm{r}}\Phi_{\mathrm{CHBA}} =$ ca. 0.0024; thirdly, the $R^*_{\mathrm{i.h.}}$ (CHBA) values were unaffected by addition of KOH, in contrast to significant effects upon $R^*_{\mathrm{i.L.}}$ (CHBA). A switch-over under high photon flux to control of $R^*_{\mathrm{i.h.}}$ (CHBA) by kinetic and efficiency limiting processes differing from those under low photon flux can be inferred from these contrasts with Fig. 1A (vide infra), but first it is important to note the qualitatively different profiles obtained

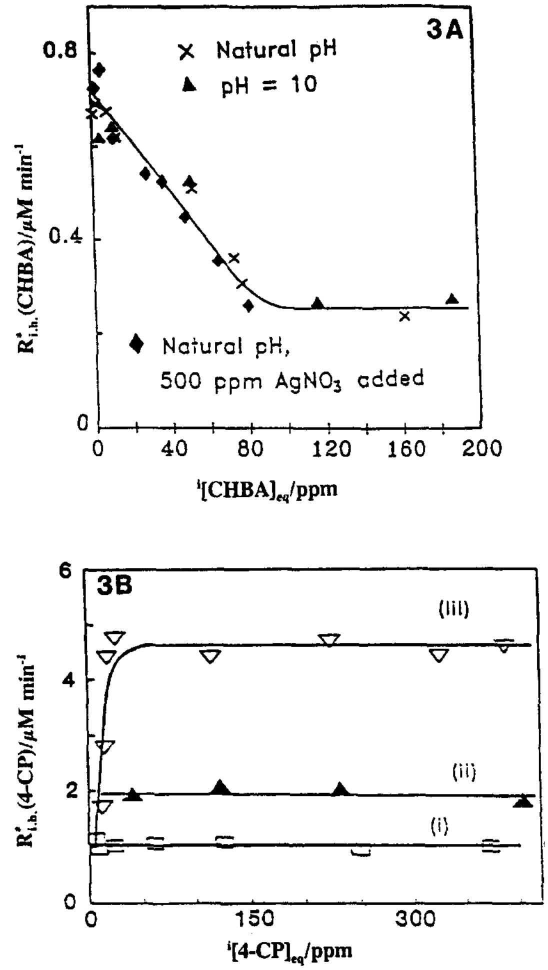

Fig. 3. Contrasting profiles as per legend to Fig. 1, but under high flux, i.e., for $R^*_{\mathrm{i.h.}}$ (CHBA) in Fig. 3A and for $R^*_{\mathrm{i.h.}}$ (4-CP) in Fig. 3B. A further notable contrast is that whereas data from CHBA/TiO$_2^*$ slurries followed the same profile regardless of change in pH to 10, or of the addition of AgNO$_3$ (cf. Fig. 3A), such addition caused an upward step change for $R^*_{\mathrm{i.h.}}$ (4-CP) as seen for plot (iii) by comparison with plots obtained without Ag$^+$ addition for aerated slurries, plot (i) and oxygenated slurries, plot (ii).

for $R^*_{\mathrm{i.h.}}$ (4-CP). Plots in Fig. 3B illustrate that in the case of poorly-adsorbing 4-CP under high flux no initial region with negative-order dependence of $R^*_{\mathrm{i.h.}}$ (4-CP) upon C_{eq} was observed for dark-preequilibrated slurries at their natural pH. Instead each of two different $R^*_{\mathrm{i.h.}}$ (4-CP) vs. C_{eq} plots for aerated and for oxygenated slurries appeared zero-order throughout the C_{eq} from 10 to 300 ppm range but with ${}^{r}\Phi_{4\text{-CP}}$ values of 9×10^{-3} and 1.7×10^{-2}, respectively. The striking contrast between this absence of any self-inhibiting effect for the poorly-adsorbing 4-CP and the strong self-inhibiting effect noted for CHBA (Fig. 3A) suggest that differences between nature and extent of adsorption of CHBA and 4-CP, or their photoproducts, onto TiO$_2$ exert a major influence upon kinetics of the TiO$_2$-photocatalysed processes under high intensity. Another difference contained within Fig. 3 and consistent with that suggestion is that 400 ppm additions of AgNO$_3$ to aerated TiO$_2$/(4-CP)$_{\mathrm{aq}}$ slurries caused an fourfold upward step change in zero-order value attainable for $R^*_{\mathrm{i.h.}}$ (4-CP)$_{\mathrm{eq}}$ in the range from 50 to 400 ppm, whereas data points on Fig. 3A show that such addition of Ag$^+$ did not significantly affect $R^*_{\mathrm{i.h.}}$ (CHBA). Bearing in mind that electron-localization by O$_2$ originating from its 15 ppm concentration in the aerated slurries could well become rate and efficiency limiting under high UV-intensity, this contrast may be understood as follows: access by Ag$^+$ to photoactive sites in the ssm remains unhindered only in the case of poorly adsorbing 4-CP (and poorly adsorbing photoproducts therefrom), thereby allowing (Ag$^+$)$_{\mathrm{ads}}$ to enhance electron localization within the ssm and freeing more photoholes to initiate photooxidation events outside the ssm of (4-CP)$_{\mathrm{aq}}$/TiO$_2^*$.

In seeking to account for other differences in the $R^*_{\mathrm{i.h.}}$ vs. C_{eq} profiles of Fig. 3 between chemisorbing CHBA and poorly-adsorbing 4-CP, preliminary consideration has been given to possible kinetic-determining roles of the following:

(A) A self-inhibiting effect upon $R^*_{\mathrm{i.h.}}$ (CHBA), originating from progressive blockage of photo-active sites on TiO$_2$ through the retention thereon of strongly-held initial products from the photo-catalytic process. Conversely, such site blockage is not significant for weakly-held products in the case of $R^*_{\mathrm{i.h.}}$ (4-CP).

(B) Slow 'surface-diffusion' of chemisorbed CHBA, or primary products therefrom, along and between the surface solution monolayers upon elementary TiO_2 particles, which are reported to exist as aggregates with overall sizes up to 5 μm in aqueous slurries. This represents a modification of the kinetic-determining role recently proposed for diffusion through the aqueous solution phase permeating the interparticle space in such aggregates [7]. Without such modification no adequate diffusion-based explanation for the differences between Fig. 3A and Fig. 3B could be envisaged.

The commercial availability of dihydroxy benzoic acids — well established as the primary products from OH radical attack on 2-hydroxybenzoic acid [8] — led us to employ the latter in experiments to test possibility (A) in respect of that HBA. Results obtained by separation and HPLC-analyses of aqueous phase aliquots from aerated $(2\text{-HBA})_{aq}/TiO_2^*$ slurries after typical high intensity illuminations at their natural pHs showed no detectable dihydroxybenzoic acid products, despite initial rates for TiO_2-sensitized removal of 2-HBA similar to those for $R^*_{i.h.}$ (CHBA) in those conditions. However, readily detectable concentrations of 2,5-dihydroxybenzoic acid — the favoured product from OH-radical attack on 2-HBA — were detected in aliquots separated and HPLC-analysed after similar illuminations of $(2\text{-HBA})_{aq}/TiO_2$ slurries having their pH adjusted to ca. 10. At first sight and when taken together with above-mentioned effects of increased pH in decreasing the extent of CHBA dark-adsorption onto TiO_2, these observations appeared consistent with the idea that for TiO_2 slurries at natural pH, the retention of strongly held primary products from PCD of HBA's could strongly modify kinetics of $R^*_{i.h.}$ (HBA). However, a corollary expected on that basis, viz. for a lower inhibiting effect in slurries at pH 10, is not borne out by the few data-points upon Fig. 3A which were obtained on such slurries at pH ca. 10. More extensive data at pH ca. 10 are desirable for rigorous test of this point.

The following basis for full rationalization of present results appears feasible by addition of modified type (B) factors to foregoing ideas concerning operation of type (A) factors in respect of the marked intensity-related alteration in R^*_i vs. C_{eq} profiles for the well-adsorbed HBA's, but not for the poorly adsorbing 4-CP. Expected manifestations of the onset of modified type (B) factors allied to type (A) include substantial changes not only in concentrations of reactant product and adsorbed oxygen within the ssm, but also in near-surface and double-layer charge within solution layers permeating the spaces between elementary TiO_2 particles. Changes of the latter type have been detected around TiO_2 particles in colloid sols by photoelectrophoretic measurements [9]. Upon establishment of such changes within the TiO_2 aggregates under illumination, the surface diffusion of chemisorbed CHBA, or products therefrom, along and between ssm's of elementary TiO_2 particles in the aggregates will be affected, especially if ionized species are involved. The nature of the $R^*_{i.m.}$ (CHBA) profiles in Fig. 2A suggest commencement of such changes after ca. 5 min. illumination of a slurry at natural pH under a flux of 5.6×10^{17} min^{-1}, but only after 20 min at pH ca. 10. Earlier onset of such effects under the higher flux of 2×10^{18} min^{-1} thus seems assured, making it likely that kinetics of $R^*_{i.h.}$ (CHBA) throughout such 'high' intensity illumination was affected by changes in type (B) factors. On the other hand, onset of such effects is unlikely to have occurred during 1–2 h illumination under the 'low' flux of 1.7×10^{16} min^{-1} thus allowing primary photooxidation events to serve as the rdp in those conditions.

Acknowledgements

The authors are grateful for financial support of this research under EC Contract STEP-0106-C and for valuable discussions with other participating laboratories. Subsequent financial support for PS as an EC-Central and Eastern European Fellow under Contract EXB-CIPA-CT-92-2232, during leave of absence from The Institute of Inorganic Chemistry, Academy of Science of Czech Republic is also acknowledged, together with technical assistance from J. Caffrey.

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