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Reactive species produced on irradiation at 365 nm of aqueous solutions of humic acids

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Abstract

In order to characterize the reactive species produced on irradiation at 365 nm of humic acid (HA) solutions, the photoinduced transformation of aromatic compounds was studied as a function of several parameters (concentrations of substrates, HA and oxygen, pH of the solution) and in the presence of additives such as isopropanol, ethylenediaminetetraacetic acid (EDTA), H_2O_2 and Fe^{2+}. No consumption of the substrates was observed in deoxygenated medium. In oxygenated solutions containing commercial HA, the rates of phenol disappearance were significant; the rate laws were dependent on the substrate and HA concentrations. In weakly oxygenated medium, the consumption rates were lower and other reactive species were involved. EDTA and citric acid led to partial inhibition of the reactions, indicating that the reactive species were related to metallic cations contained in HA. In acidic solution, hydroxyl radicals were produced by a photo-Fenton reaction. HA synthesized from phenol was incapable of photoinducing the transformation of the substrates, whereas HA synthesized from phenol–Fe^{3+} produced transformation of the substrates. The formation of singlet oxygen on irradiation of commercial HA was characterized previously. Unexpectedly, no consumption of phenolic substrates through singlet oxygen reaction was observed.

Keywords: Humic acid; Reactive species; Aqueous medium; Phenols

1. Introduction

Photochemical transformations are important in the abiotic degradation of organic chemicals in the soil and aquatic environments. Humic substances, which are ubiquitous natural organic materials, strongly absorb sunlight and may therefore photoinduce the transformation of non-absorbing organic chemicals.

The numerous studies undertaken so far have shown that humic materials (polyphenolic compounds with multiple carboxyl, carbohydrate and peptide moieties) act as sensitizers or precursors for the production of reactive intermediates [1–3]. Some of these intermediates have been clearly identified ($^1O_2$ [4–6], e_{aq}^- [7–9], $O_2^{\bullet -}$ [10,11], H_2O_2), but many others remain unknown. Peroxyl-type radicals were thought to be responsible for the degradation of phenol derivatives [12,13], but a recent study has shown that these reactions could be due to reactive triplet states [14]. The photochemical reactivity of humic substances is complex, depending on the experimental conditions under which studies are performed and, in particular, on the excitation wavelength. However, the origin of the humic material does not greatly influence the results, indicating that the photoinductive properties arise from widely found chromophores.

The purpose of this work was to characterize the reactive species produced on excitation of humic acids (HAs) at $\lambda > 300$ nm. To obtain more information on these species, the photoinduced transformation of aromatic compounds was studied as a function of several parameters: the concentrations of the reactants, pH and influence of additives such as hydroxyl radical scavengers or metallic cation complexants. The photoinductive properties of commercial HA (Aldrich) were studied at 365 nm and compared with those of HAs synthesized from phenols.

2. Experimental details

2.1. Materials and methods

All reagents were of the highest grade available and were used as received, with the exception of furoin which was recrystallized from water. Water was purified with a Millipore Milli-Q device.

Solutions were irradiated at 365 nm in a water-cooled reactor using three black lamps (HPW 125 W, Philips). Monochromatic irradiations were performed with a Bausch and Lomb monochromator equipped with a high-pressure mercury lamp. Ferrioxalate was used as chemical actinometer.

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High performance liquid chromatography analyses have been described elsewhere [9]. Deoxygenation of the solutions was performed by three freeze–pump–thaw cycles on a vacuum line.

2.2. Synthesis of HAs

HAs were synthesized by irradiating at 254 nm oxygen-saturated solutions containing phenol (40 g l^{-1}) alone or in the presence of $Fe(ClO_4)_3$ (0.8 g l^{-1}), benzoquinone (10 g l^{-1}) or 4-methylcatechol (20 g l^{-1}). The HAs were recovered as described previously [9]. The results of the elemental analyses are as follows: HA (Aldrich) (C, 41.9%; H, 4.1%; O, 50.4%; Fe, 1.25%); HA from phenol (C, 63.0%; H, 4.4%; O, 32.4%); HA from phenol–Fe^{3+} (C, 64.2%; H, 4.1%; O, 29.4%; Fe, 1.0%); HA from benzoquinone (C, 58.9%; H, 4.0%; O, 37.1%); HA from 4-methylcatechol (C, 64.4%; H, 5.0%; O, 30.6%). The HAs were treated with ammonia to convert carboxylic acids into carboxylate ions. The IR absorption band at 1710 cm^{-1} observed before NH_3 treatment and characteristic of the C=O stretching vibration of carboxylic acids was replaced after treatment by an absorption band between 1600 and 1520 cm^{-1}. From the decrease in the intensity of the band at 1710 cm^{-1}, the carboxyl content was evaluated to be 1.1 meq g^{-1} for HA (Aldrich) and 0.8 meq g^{-1} for HA from phenol.

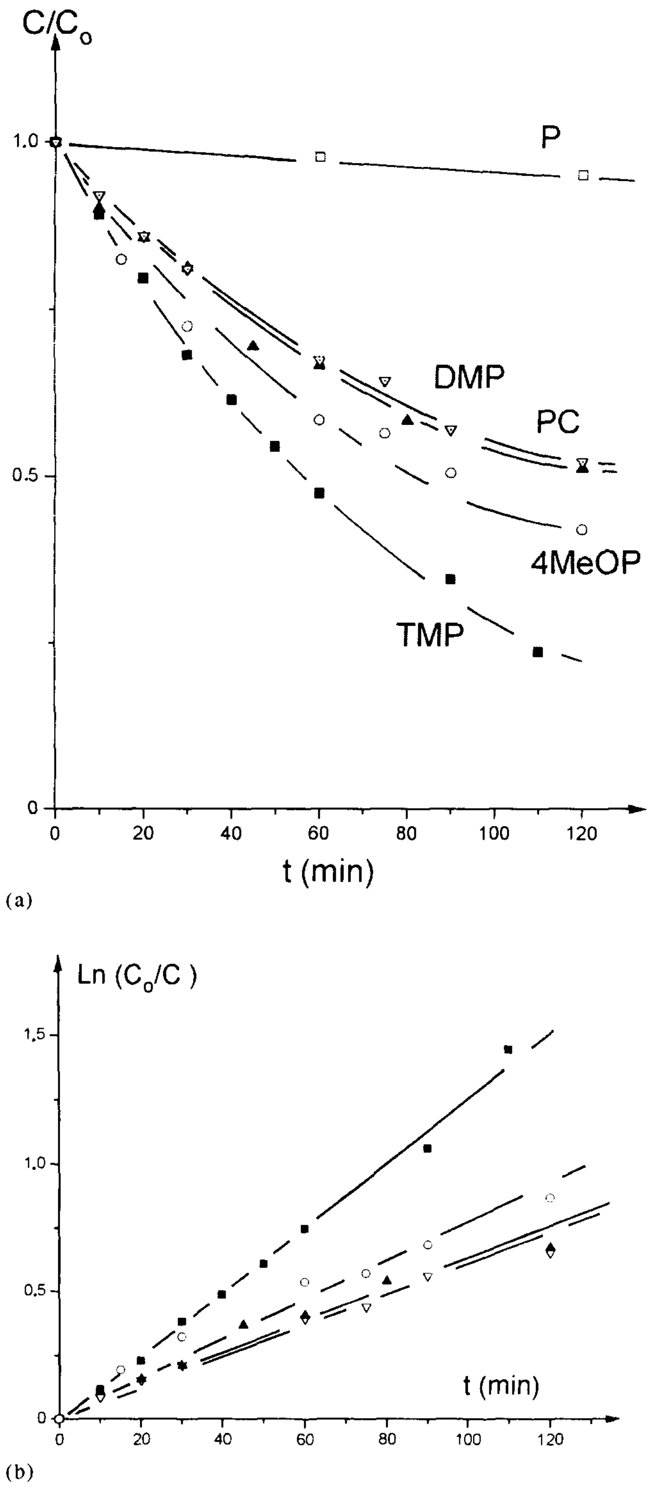


Fig. 1. (a) Kinetics of phenol disappearance on irradiation of oxygen-saturated solutions containing HA (Aldrich) (0.1 g l^{-1}) and substrates (2×10^{-5} M) (pH 6.5): TMP, 2,4,6-trimethylphenol; 4MeOP, 4-methoxyphenol; PC, pyrocatechol; DMP, 2,6-dimethylphenol; P, phenol. (b) Plot of $\ln(C_0/C)$ vs. time.

3. Results

3.1. Influence of substrates and HA concentration

The transformation of phenolic substrates (2×10^{-5} M) induced by excitation of HA (Aldrich) (0.1 g l^{-1}) was studied in oxygen-saturated solutions buffered at pH 6.5 by phosphates. The kinetics of substrate consumption are shown in Fig. 1. Plots of $\ln(C_0/C)$ vs. time are linear, indicating that the rate laws are first order with respect to the substrates. The values of the apparent first-order rate constants K increase with the oxidizability of the substrates (see Table 1).

The initial rates of 2,4,6-trimethylphenol (TMP) consumption were measured as a function of TMP and HA concentrations in air-saturated solutions. The dependence of $-\mathrm{d}[\mathrm{TMP}]/\mathrm{d}t$ on the HA concentration (m_{HA}) is given in Table 2 and experimental data of $(-\mathrm{d}[\mathrm{TMP}]/\mathrm{d}t)^{-1}$ measured for $m_{HA}=0.1$ g l^{-1} are plotted vs. $[\mathrm{TMP}]^{-1}$ in Fig. 2. From these results, we can deduce the rate law of TMP disappearance as

$$-\mathrm{d}[\mathrm{TMP}]/\mathrm{d}t = 0.0069 I_a^{HA} \frac{[\mathrm{TMP}]}{[\mathrm{TMP}]+8.3\times10^{-3} m_{HA}+3.0\times10^{-4}}$$

where I_a^{HA} is the light absorbed by HA and m_{HA} is expressed in grams per litre. The values of the TMP consumption rate calculated using this relationship are in good agreement with the experimental values (see Table 2). At low TMP concentrations, the rate of TMP disappearance is first order with respect to the TMP concentration and K depends on the HA

Table 1
Values of the apparent first-order rate constant K (m_{HA} = 0.1 g l^{-1}, pH 6.5, $C_0 = 2\times10^{-5}$ M)

	Substrate				
	TMP	4MeOP	PC	DMP	P
K (s^{-1})	2.4×10^{-4}	1.1×10^{-4}	9.2×10^{-5}	9.2×10^{-5}	7.9×10^{-6}

Table 2
Initial rates of TMP consumption as a function of m_{HA}: experimental data and calculated values (see text)

[TMP] (M)	m_{HA} (g l^{-1})	I_a^{HA} (einstein l^{-1} s^{-1})	$-$d[TMP]/dt_{exp} (M s^{-1})	$-$d[TMP]/dt_{cal} (M s^{-1})
1.0×10^{-3}	0.029	6.8×10^{-7}	3.9×10^{-9}	3.1×10^{-9}
1.0×10^{-3}	0.10	1.3×10^{-6}	5.7×10^{-9}	4.2×10^{-9}
1.0×10^{-3}	0.10	4.8×10^{-5}	1.7×10^{-7}	1.6×10^{-7}
1.0×10^{-3}	0.28	5.3×10^{-5}	1.0×10^{-7}	1.1×10^{-7}
2.0×10^{-5}	0.004	1.2×10^{-7}	4.0×10^{-11}	5.3×10^{-11}
5.0×10^{-5}	0.004	1.2×10^{-7}	1.7×10^{-10}	1.3×10^{-10}

concentration if $m_{HA} > 0.003$ g l^{-1}. At high TMP concentrations, the rate of TMP consumption is constant.

3.2. *Influence of oxygen concentration*

In deoxygenated solutions, no reaction occurs (Fig. 3(a)). The initial rates of TMP consumption are the same in air-saturated solutions ($[O_2] = 2.6\times10^{-4}$ M) and oxygen-saturated solutions ($[O_2] = 1.3\times10^{-3}$ M) at all concentrations of TMP and HA. In initially air-saturated solutions, the consumption of TMP is rapid until the disappearance of about 2.5×10^{-4} M of TMP. Then the rate of consumption slows down, becoming constant (Fig. 3(b)). The rate of TMP transformation increases again if oxygen is introduced. These results can be explained as follows: in the first part of the curve, oxygen is consumed, and in the second part, diffusion of oxygen in the solution allows the reaction to continue. In oxygen-saturated solutions, the consumption of TMP seems unlimited, suggesting that the chromophores responsible for the formation of the reactive species are not destroyed during irradiation (Fig. 3(c)).

3.3. *Influence of pH*

In oxygen-saturated solutions, the kinetics of TMP consumption are the same at pH 6.5 and 3.6. A pH effect is found in initially air-saturated solutions: the rate of transformation in the linear part of the curve is higher at pH 3.6 than at pH 6.5 (Fig. 4). This difference is suppressed when a hydroxyl radical scavenger such as isopropanol is added to the solution. Hydroxyl radicals are thus produced in acidic medium. Such a formation is not observed in solutions containing HA concentrations lower than 0.01 g l^{-1}.

3.4. *Influence of metallic cation complexants*

In order to obtain a better insight into the role of metallic cations in the photoinductive properties of HAs, citric acid and ethylenediaminetetraacetic acid (EDTA) were added to the solutions. When irradiations are performed in oxygen-

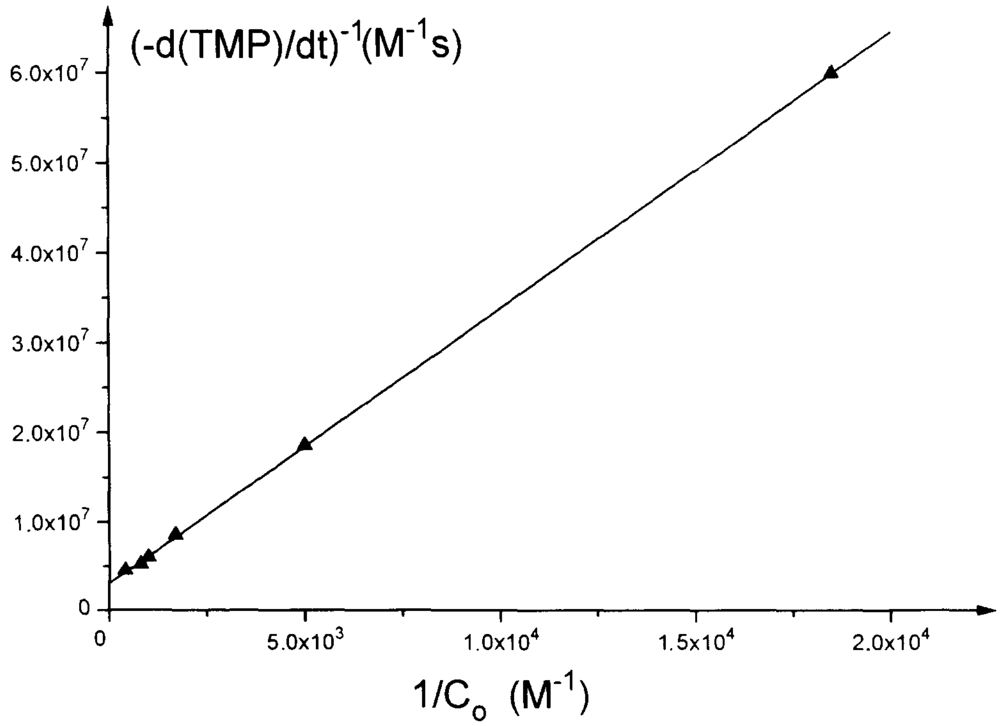


Fig. 2. Plot of $-(\mathrm{d}[TMP]/\mathrm{d}t)^{-1}$ vs. $[TMP]^{-1}$; m_{HA} = 0.1 g l^{-1}.

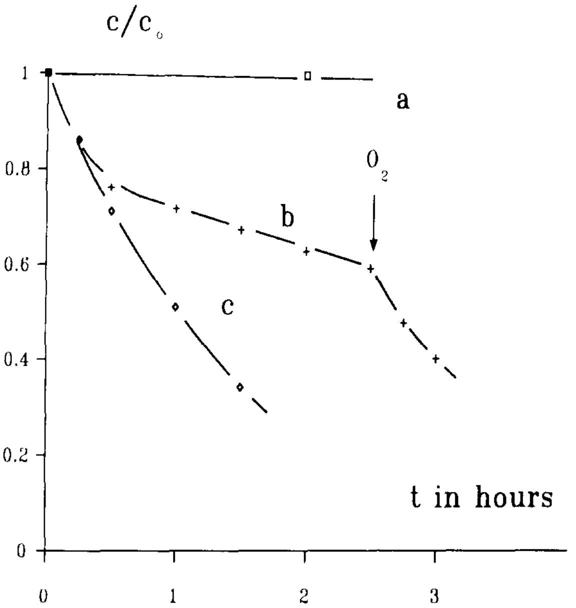


Fig. 3. Influence of oxygen on the kinetics of TMP disappearance (HA (Aldrich), 0.1 g l^{-1}; pH 6.5): (a) deoxygenated solution; (b) initially air-saturated solution; (c) oxygen-saturated solution.

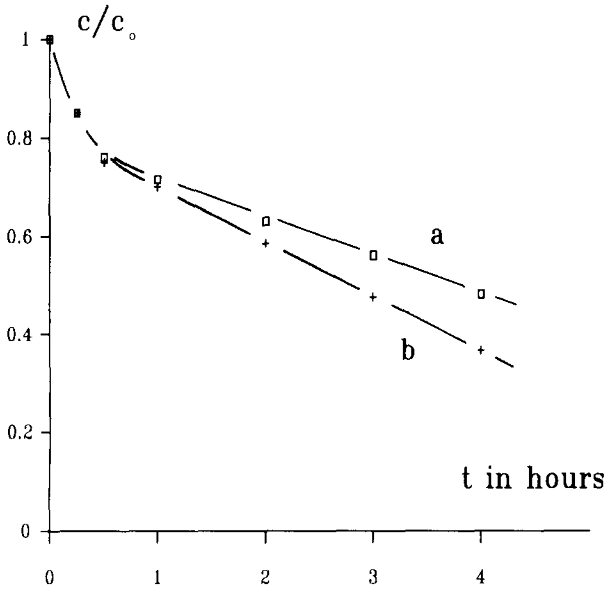


Fig. 4. Effect of pH on the kinetics of TMP consumption: (a) pH 6.5; (b) pH 3.6.

saturated solutions, these additives (1.5×10^{-4} M) have no effect on the consumption of TMP. An inhibiting influence is observed in initially air-saturated solutions buffered at pH 6.5 (Fig. 5). In acidic medium, the inhibiting effect disappears.

EDTA has no effect on the consumption of phenol or 4-methoxyphenol in neutral or acidic medium.

3.5. Influence of H_2O_2 and Fe^{2+}

The transformation of fenuron (1,1-dimethyl-3-phenylurea) (2×10^{-4} M), photoinduced by excitation of HA (Aldrich) in acidic medium, is slow. When H_2O_2 and Fe^{2+} are added to the solution, a significant increase in the rate is found (see Fig. 6).

3.6. Involvement of singlet oxygen

It was previously shown that excitation of HA (Aldrich) produces singlet oxygen. The quantum yields of production under our experimental conditions were evaluated to be 0.002 in air-saturated solution and 0.0045 in oxygen-saturated medium [9]. On the other hand, phenols are known to react with singlet oxygen with rate constants of 2.6×10^{6} M^{-1} s^{-1} for phenol [15] and 6.2×10^{7} M^{-1} s^{-1} for TMP [16]. On

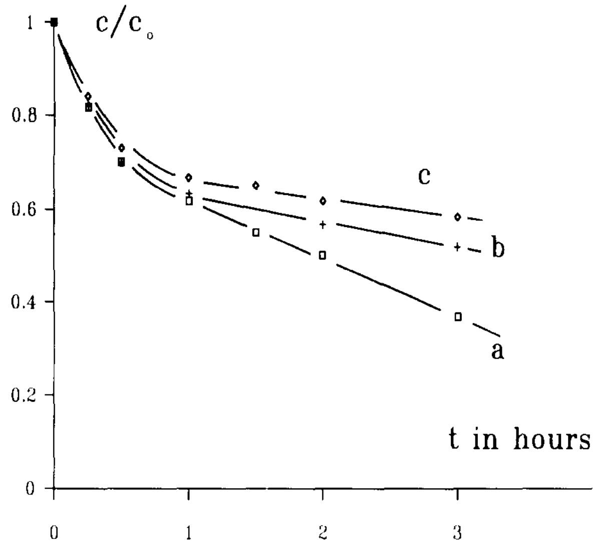


Fig. 5. Influence of EDTA and citric acid on the kinetics of TMP disappearance (HA (Aldrich), 0.1 g l^{-1}; pH 6.5): (a) absence of additive; (b) [EDTA] $=1.5\times10^{-4}$ M; (c) [citric acid] $=1.5\times10^{-4}$ M.

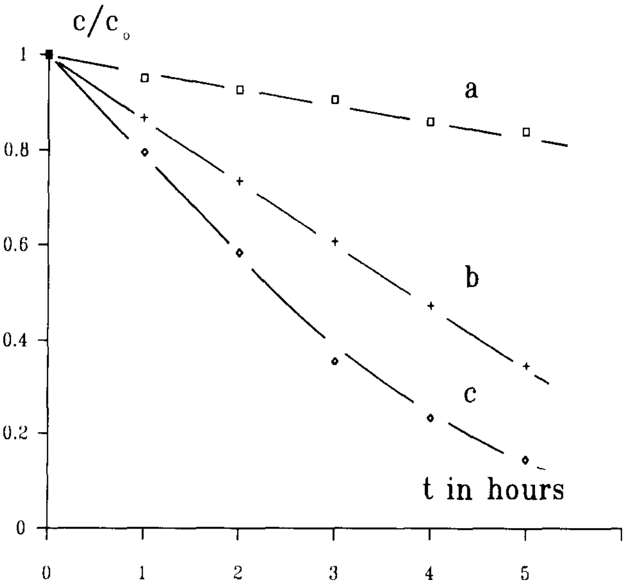
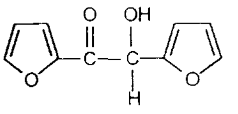


Fig. 6. Influence of H_2O_2 and Fe^{2+} on the kinetics of fenuron disappearance (HA (Aldrich), 0.1 g l^{-1}; pH 6.5): (a) absence of additive; (b) $[H_2O_2]=5\times10^{-4}$ M; (c) $[Fe^{2+}]=5\times10^{-4}$ M.

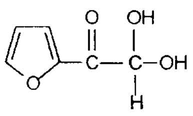
Table 3
Influence of N_3^- and TMP on the rate of FDE formation on irradiation of solutions containing HA (Aldrich) and furoin

Additive (M)	d[FDE]/d*t* (M s^{-1})
None	1.6×10^{-8}
N_3^- (5×10^{-4})	8.8×10^{-9}
TMP (10^{-3})	3.6×10^{-9}
N_3^- + TMP	2.0×10^{-9}

the basis of these values, the consumption of TMP through singlet oxygen reaction should represent 14% and 32% of the total transformation in air- and oxygen-saturated solutions respectively. For phenol, the value should be at least twofold higher than that measured. Therefore it is concluded that the reaction through singlet oxygen is less important than expected. Indeed, singlet oxygen scavengers such as azide anion have no influence on phenol consumption. This result was previously mentioned by Faust and Hoigne [13]. To understand better why phenols do not react with singlet oxygen, we have studied the influence of TMP on the photoinduced transformation of furoin, a substrate which readily reacts with singlet oxygen to yield a specific product (FDE) [5].



furoin



FDE

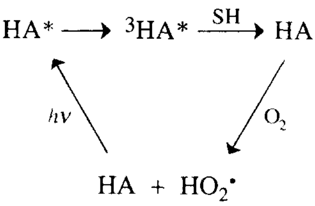
The results are reported in Table 3. The rate of FDE formation is significantly inhibited by N_3^- and TMP.

3.7. Comparison with synthesized HA

The photoinductive properties of HAs synthesized from phenol or phenol derivatives were also studied. The rate of TMP (10^{-3} M) disappearance is about 20 times lower on irradiation of these HA species than on irradiation of HA (Aldrich). With HA synthesized from phenol–Fe^{3+} mixtures, the rate of TMP consumption is twofold higher and is enhanced in acidic medium; isopropanol partly inhibits the consumption of TMP in acidic solution, whereas no effect is observed at pH 6.5 (Fig. 7). Moreover, EDTA and citric acid inhibit almost completely the transformation of TMP at pH 6.5. These results are similar to those found in weakly oxygenated solutions of HA (Aldrich).

4. Discussion

Several reactive species are involved in the transformation of the substrates studied. The most efficient are not influenced by pH, isopropanol or EDTA. The chromophores responsible for the formation of these species seem to be regenerated in oxygenated solutions. As previously proposed by Canonica and Hoigne [14], excited triplet states could react directly with the substrates, the oxygen effect being explained by the following mechanism



From the rate law of TMP consumption, it can be deduced that the reactive species also react with HA and through a third pathway which does not depend on the oxygen concentration for $[O_2] > 2.6\times10^{-4}$ M. If we assume that the reactive species are triplet states, the third pathway could be a deactivation process. Canonica and Hoigne [14] suggested that carbonyl-type chromophores could be responsible for this photoreactivity. Structural studies have shown that humic and fulvic acids contain about one ketone group per monocyclic aromatic ring, aromatic ketone groups being the majority [17]. However, every site undergoing photoreduction could be involved.

Other oxidant species are involved which are less reactive. They only react with TMP. Their rates of reaction with TMP can be measured when the production of the previous species is drastically limited because of a very low oxygen concentration. The presence of EDTA or citric acid prevents the formation of these reactive species. Therefore it is suggested that the formation of these intermediates is related to the metallic cation content in the HA structure and most probably to that of Fe^{2+}/Fe^{3+}. HAs form very stable complexes with iron. Chelate rings involving adjacent COOH and phenolic

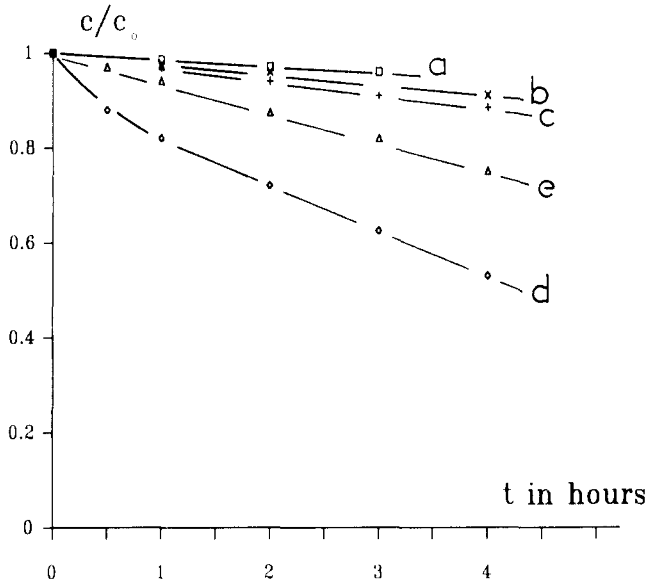


Fig. 7. Kinetics of TMP consumption on irradiation of synthesized HA: (a) HA from phenol, pH 6.5; (b) HA from phenol, pH 3.6, with or without isopropanol; (c) HA from phenol + Fe^{3+}, pH 6.5; (d) HA from phenol + Fe^{3+}, pH 3.6; (e) HA from phenol + Fe^{3+}, pH 3.6, in the presence of isopropanol.

OH groups or two adjacent COOH groups are thought to be formed [18]. On irradiation, an oxid–reduction can occur

$$Fe^{3+}\text{–HA} \xrightarrow{h\nu} Fe^{2+} + \text{free radical}$$

creating Fe^{2+} [19] and weakly oxidizing free radicals. In neutral medium, Fe^{2+} is readily converted into Fe^{3+} by reaction with O_2. In acidic solutions, Fe^{2+} is probably oxidized by H_2O_2 formed by disproportionation of $O_2^{\bullet -}/HO_2^{\bullet}$, and hydroxyl radicals are generated

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^-$$

When H_2O_2 is added to acidic solutions, the rate of $OH^{\bullet}$ formation is significantly increased. Assuming that all the $OH^{\bullet}$ radicals react with the substrate and that the rate of the Fenton reaction, under these conditions, is limited by the rate of Fe^{2+} production, the apparent quantum yield of Fe^{2+} formation is evaluated as 1.3×10^{-4}. In the same way, the addition of Fe^{2+} also enhances the rate of $OH^{\bullet}$ formation.

Phenolic compounds do not disappear through singlet oxygen reaction. These substrates can deactivate singlet oxygen or the triplet states responsible for the production of singlet oxygen.

On excitation at 254 nm, synthetic and commercial HA exhibit similar photoinductive properties [9]. This result leads to the conclusion that the phenolic moiety is responsible for the photoreactivity at short wavelengths. The photochemical behaviour observed on excitation at 365 nm is very different, indicating that other chromophores are involved. Similarities found between HA (Aldrich) and HA synthesized from phenol–Fe^{3+} confirm that iron plays a role in the photoreactivity of HA.

References

[1] W.J. Cooper, R.G. Zika, R.G. Petasne and A.M. Fisher, *Adv. Chem. Ser., 219* (1989) 349.
[2] J. Hoigne, B.C. Faust, W.R. Haag, F.E. Scully and R.G. Zepp, *Adv. Chem. Ser., 219* (1989) 363.
[3] R.G. Zepp, P.F. Scholtzhauer and R.M. Sink, *Environ. Sci. Technol., 19* (1985) 74.
[4] W.R. Haag and J. Hoigne, *Environ. Sci. Technol., 20* (1986) 341.
[5] J.-P. Aguer and C. Richard, *Toxicol. Environ. Chem., 39* (1993) 217.
[6] F. Frimmel, H. Bauer, J. Putzien, P. Murasecco and A.M. Braun, *Environ. Sci. Technol., 21* (1987) 541.
[7] R.G. Zepp, A.M. Braun, J. Hoigne and J.A. Leenheer, *Environ. Sci. Technol., 21* (1987) 485.
[8] J.F. Power, D.K. Sharma, C.H. Cooper, R. Bonneau and J. Joussot-Dubien, *Photochem. Photobiol., 44* (1986) 11.
[9] J.-P. Aguer and C. Richard, *J. Photochem. Photobiol. A: Chem., 84* (1994) 69.
[10] R.M. Baxter and J.H. Carey, *Nature, 306* (1983) 575.
[11] W.J. Cooper and R.G. Zika, *Science, 220* (1983) 711.
[12] T. Mill, D.G. Hendry and H. Richardson, *Science, 207* (1980) 886.
[13] B.C. Faust and J. Hoigne, *Environ. Sci. Technol., 21* (1987) 957.
[14] S. Canonica and J. Hoigne, *Environ. Sci. Technol.*, in press.
[15] P.G. Tratnyek and J. Hoigne, *Environ. Sci. Technol., 25* (1991) 1596.
[16] P.G. Tratnyek and J. Hoigne, *J. Photochem. Photobiol. A: Chem., 84* (1994) 153.
[17] J.A. Leenheer, M.A. Wilson and R.L. Malcolm, *Org. Geochem., 11* (1987) 273.
[18] S.A. Boyd, L.E. Sommers and D.W. Nelson, *Soil Sci. Soc. Am. J., 45* (1981) 1241.
[19] C.J. Miles and P.L. Brezonik, *Environ. Sci. Technol., 15* (1981) 1089.