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Wat. Res. Vol. 34, No. 4, pp. 1119–1126, 2000
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Printed in Great Britain
0043-1354/00/\$ - see front matter

PII: S0043-1354(99)00254-7

KINETICS OF PHOTODEGRADATION OF THE FUNGICIDE FENARIMOL IN NATURAL WATERS AND IN VARIOUS SALT SOLUTIONS: SALINITY EFFECTS AND MECHANISTIC CONSIDERATIONS

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(First received 1 November 1998; accepted in revised form 1 May 1999)

Abstract—The rate of photodegradation of the fungicide fenarimol (α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidine-methanol) by solar radiation has been studied in natural waters with different salinities. Photodegradation rates and quantum yields are found to decrease with increasing salinity.

To explain this behaviour, experiments were performed with different salt solutions (NaCl, NaBr, BaCl₂ and ZnCl₂) using both solar irradiation and a photoreactor (λ_{excit} 313 nm). As with natural waters, marked effects of added salt were observed on the photolysis rate, which decreased significantly from 0.67 h⁻¹ in the absence of salt to 0.11 h⁻¹ in the presence of BaCl₂. In photoreactor studies, the observed order of quenching was BaCl₂ > ZnCl₂ and NaBr > NaCl. In contrast, neither the triplet state quencher sorbic acid nor oxygen had any effect on the photolysis, supporting the idea that photodegradation goes by the lowest excited singlet state of fenarimol.

To understand the origin of the effect of added salts, fluorescence quenching studies have been performed with various halide and nonhalide salts and the respective quenching constants determined. With NaCl and NaBr, the ratio of fluorescence quenching constants is identical to the ratio of reciprocal quantum yields for photodegradation of fenarimol, indicating a common mechanism. The correlation of fluorescence quenching rates with halide ion oxidation potentials strongly suggests that this involves an electron transfer mechanism. It is suggested that the effect may be used to stabilise the fungicide towards photodegradation. © 2000 Elsevier Science Ltd. All rights reserved

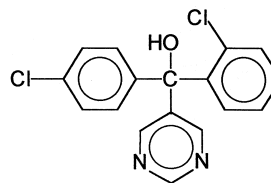
Key words—fenarimol, kinetics of photodegradation, salinity effect

INTRODUCTION

Fenarimol — α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidine-methanol (I) — is an extensively used fungicide which is composed of two chlorobenzene and one pyrimidine rings, connected by a carbinol group. Whilst it has long been known that this compound readily breaks down in sunlight (Worthing, 1983), there is little published information on its photostability under environmental conditions. In a previous report (Mateus *et al.*, 1997) we presented a spectroscopic study of the fungicide, showing that the lowest excited singlet state, corresponding to an absorption between 280 and 330 nm, is localised on the pyrimidine ring and has n,π^* character. This overlaps with the solar emis-

sion spectrum and is expected to play a dominant role in the photodegradation processes of this fungicide under natural environmental conditions (Mateus *et al.*, 1994).

In this report, we extend the study on the relationship between the photochemical degradation of fenarimol and its lowest excited ¹(n,π^*) state, with emphasis the kinetics of photodegradation and on the action of certain chemical agents on its photostability. Mechanistic suggestions for the observed effects are also presented.



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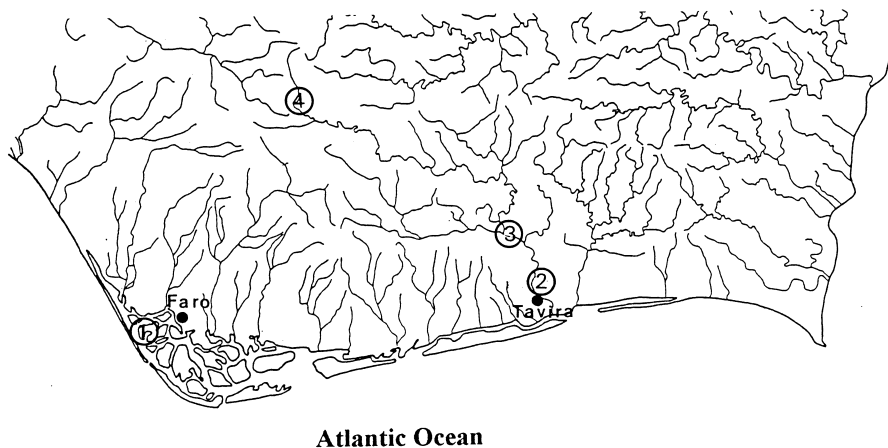


Fig. 1. Hydrographic map of the study area showing the sampling sites for the natural waters used in the photodegradation studies: (1) Ria Formosa (lagoon), (2) Rio Gilão (river at a intertidal zone), (3) Rio Séqua (watercourse), (4) Ribeira de Alportel (watercourse).

EXPERIMENTAL SECTION

Photodegradation studies were carried out using either sunlight or a "merry-go-round" photoreactor, fitted with a medium pressure mercury lamp (400 W).

For solar irradiation studies, kinetic experiments were followed during spring, fall and winter at Faro localized in the south of Portugal, at sea level (37°N 9°W). Actinometry was carried out using a solution of p-nitroacetophenone (10^{-5} M) and different concentrations of pyridine (0.042 M for winter and 0.093 M for spring) (Dulin and Mill, 1982). 100 ml crystallisation dishes were filled with fenarimol solutions (5 mg/L) in distilled water, in several chemically characterised natural waters (Fig. 1), and in aqueous solutions with and without different additives (NaCl, NaBr (both 0.5 M) and sorbic acid (1 mM at pH 7)). The analytical methods have been described in a previous paper (Mateus *et al.*, 1994).

With the photoreactor studies, the 313 nm mercury line was employed, using an aqueous solution of potassium chromate and sodium carbonate as a filter (Leifer, 1988). Fenarimol samples in aerated and deaerated (argon bubbling during 15 min) distilled water, in different aqueous salt solutions (NaCl, NaBr, BaCl₂, ZnCl₂, ZnSO₄, all 0.5 M) and in aqueous sorbic acid solution (1 mM) were irradiated and analysed according to the previously described methodology (Mateus *et al.*, 1994).

For fluorescence quenching studies, fenarimol solutions (1.2 mM) were prepared in methanol/water 50/50 (v/v) at different salt concentrations (Table 1).

The emission spectra were registered on a Jasco-777 Spectrofluorimeter, with excitation at 295 nm and observation of fluorescence around 370 nm. For Stern-Volmer plots, spectral areas were calculated and the intensity ratio was obtained by comparison with the spectral area of a standard fenarimol solution in methanol/water. Good linear plots were observed in all cases, from which the Stern-Volmer constants, K_{SV} , were calculated.

The fluorescence lifetime of the standard fenarimol solution was measured on an Edinburgh Instruments FL 9000 Fluorometer using a nitrogen gas discharge lamp for excitation at 295 nm, with observation of fluorescence at

370 nm. Results were confirmed using a ps time resolution single photon counting system with cavity dumped dye laser (coherent 7013) pumped by a mode locked Nd:YAG laser (coherent 76 s) at the "Instituto Superior Técnico", Lisbon. A total of 10,000 counts was used, with excitation at 300 nm and observation at 370 nm.

The half-wave potential of a standard solution of fenarimol in methanol/water (50/50 v/v), was determined by differential polarography using a Metrohm 647A Stard polarograph with a mercury drop electrode and using a reference electrode of Ag/AgCl.

RESULTS AND DISCUSSION

Photodegradation kinetic studies

The kinetics of photodegradation of fenarimol by solar irradiation in chemically characterised natural waters was studied by monitoring its loss by HPLC with UV detection. The experimental results, together with those for distilled water, are presented in Fig. 2(a,b). Rate constants for photodegradation were calculated from the slopes of these plots and relative photodegradation quantum yields compared with distilled water (taking a hypothetical reference value $\phi = 1$) are given, together with analytical data on the natural waters, in Table 2. Similar behaviour was observed with deaerated and aerated solutions, showing that molecular oxygen has no effect on the initial photochemical process. However, it can clearly be seen that k_{dp} values are reduced to 1/3 of that in distilled water, when the salinity increases to 35.6‰ (typical sea water salinity).

The lack of effect of oxygen strongly suggests that photodegradation does not involve fenarimol triplet state. To check this, photolysis was carried out both with sunlight and the photoreactor, using the strong triplet excited state quencher sorbic acid[†] (Figs 3 and 4 respectively). No effect was observed on the rate, confirming that reaction does not proceed by a triplet pathway, but most probably

[†]Whilst we do not have a value for the triplet energy of sorbic acid, it must be very close to that of the related octa-2,4,6-trienal ($15\,210\text{ cm}^{-1}$ (Evans, 1960)).

Table 1. Fluorescence quenching studies^a

Salt	Concentration (M)	K_{SV} (M^{-1})	k_q ($M^{-1}ns^{-1}$)
NaCl	0.25–0.5–0.75–1	0.44 ± 0.04	1.19
NaBr	0.125–0.25–0.375–0.5	0.90 ± 0.06	2.44
NaI	0.125–0.25–0.375–0.5	2.22 ± 0.15	6.0
NaSCN	0.0625–0.125–0.25–0.5	2.21 ± 0.07	5.98
Na ₂ SO ₄ ·10H ₂ O	saturated solution	0	0
CsCl	0.25–0.5–0.75–1	0.69 ± 0.07	1.88
ZnCl ₂	0.0625–0.125–0.25–0.5	0.75 ± 0.03	2.02
ZnSO ₄	0.252–0.504–1–2	0	0
SrCl ₂	0.0625–0.125–0.25–0.5	1.51 ± 0.04	4.09
BaCl ₂	0.0625–0.125–0.25–0.5	1.63 ± 0.04	4.41

^a K_{SV} = Stern–Volmer constants; k_q = quenching constants calculated with $\tau = 0.37$ ns.

involves the lowest excited singlet state of fenarimol.

To see whether the observed salinity effect is related to the quenching of the singlet excited state of the fungicide, the studies on solar photolysis using natural waters were complemented using aqueous salt solutions of NaCl and NaBr (both 0.5 M). Results are presented in Table 3 and Fig. 3, and it is clearly seen that the halide ions significantly slowed down the rate of photolysis, with $Br^- > Cl^-$. It has long been known that halide ions act as good quenchers of fluorescence of aromatic molecules (Beer *et al.*, 1970; Watkins, 1974), and these results suggest that photodegradation reaction may be going through the fenarimol singlet state.

Both electron-transfer and heavy atom effect mechanisms may be involved in such quenching. To obtain more information, these experiments were repeated using the 313 nm line of a photoreactor for irradiation and extended to solutions of ZnCl₂, ZnSO₄ and BaCl₂, (Table 4 and Fig. 4). Although the results obtained were only in qualitative agreement with those using sunlight, they confirm the general ideas on the dependence of the photodegradation on the tested salt. The absence of any effect of zinc(II) sulfate shows that with ZnCl₂, only Cl⁻ contributes significantly to the quenching. Although the total chloride ion concentration in this case is twice that with the NaCl solution (0.5 M), the photodegradation rates are identical. However, this can readily be explained by considering the known complexing of zinc(II) and chloride ions under

these conditions (Short and Morris, 1961; Morris *et al.*, 1963), which will reduce the free Cl⁻ concentration. With barium(II) chloride, which is known to be fully dissociated under these conditions (Righellato and Davies, 1930), a stronger quenching effect is observed, in agreement with the higher free chloride ion concentration. With both the zinc(II) and barium(II) salts, little effect of the cation is observed, suggesting that heavy atom effects on the photodegradation are not significant. As heavy atoms are known to promote triplet formation by enhanced intersystem crossing (McGlynn *et al.*, 1969), this lack of a heavy atom effect on the photolysis provides further support for a dominant mechanism involving the singlet excited state.

Fluorescence quenching studies

To obtain further information on the quenching mechanism, fluorescence spectra were measured of solutions of fenarimol in methanol–water solution (50/50 v/v) in the presence of various halide and nonhalide salts. The effect of the anion was studied by using a series of sodium salts, whilst various metal chlorides were used to see the dependence on the nature of the cation.

No fluorescence quenching was observed with sodium or zinc sulfate. Quenching was observed with all the other salts, and the data obeyed the Stern–Volmer equation:

$$\frac{I_f^0}{I_f} = 1 + k_q \tau_{exp}[Q].$$

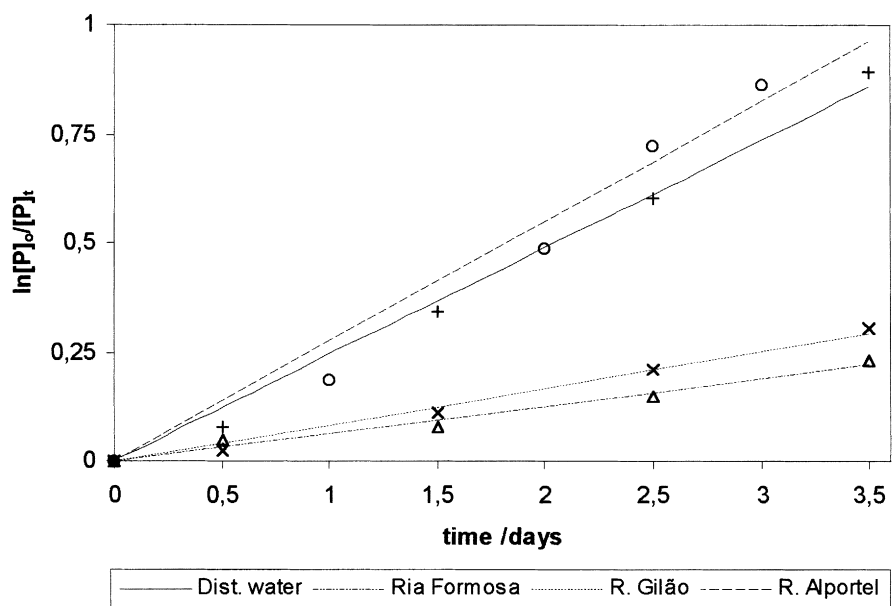
Table 2. Solar photodegradation rate of fenarimol in chemically characterised natural waters

Fenarimol solutions	PO ₄ ³⁻ (μM)	NO ₃ ⁻ (μM)	pH	Salinity (‰)	k_{dp} (days ⁻¹)		ϕ_{rel}^c
					winter ^a	spring	
Distilled water	–	–	–	–	0.24 ± 0.01	0.32 ± 0.03	1
R. Alportel	0.13	55	6.2	≈ 0	0.26 ± 0.03	0.39 ± 0.01	≈ 1.1
R. Séqua	4.4	90	7.2	≈ 0		0.37 ± 0.01	≈ 1.1
R. Gilão ^b	0.68	10	7.8	25.4	0.088 ± 0.010		≈ 0.37
Ria Formosa	0.55	1.4	7.9	35.6	0.060 ± 0.010	0.10 ± 0.01	≈ 0.3

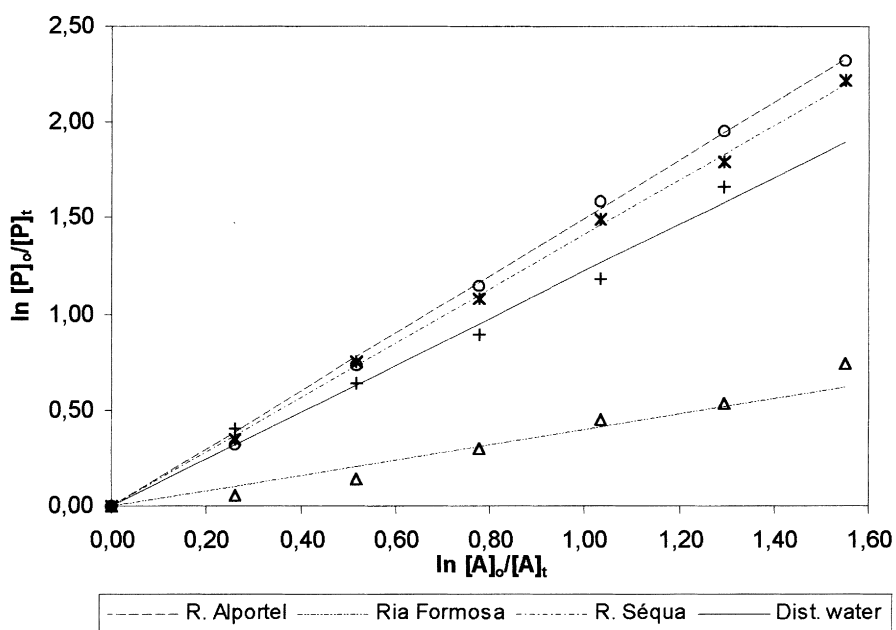
^aExperiments made in quartz tubes.

^bIntertidal zone.

^cRelative quantum yield compared with distilled water.



a



b

Fig. 2. Comparative study of fenarimol sunlight photodegradation in distilled water and different natural waters (Ria Formosa (lagoon), Rio Gilão (river), Rio Séqua (watercourse), Ribeira de Alportel (watercourse)): (a) Variation of fungicide concentration with time of irradiation. (b) Variation of fungicide concentration relative to actinometer concentration, as a function of irradiation time.

Stern–Volmer constants (K_{SV}) were determined from the slopes of plots of fluorescence intensity ratio against quencher concentration, and respective fluorescence quenching rate constants (k_q) calcu-

lated from these using the fluorescence lifetime of fenarimol measured in this solvent (Table 1).

Quenching of excited states by halide anions may occur either by an electron transfer reaction (Beer

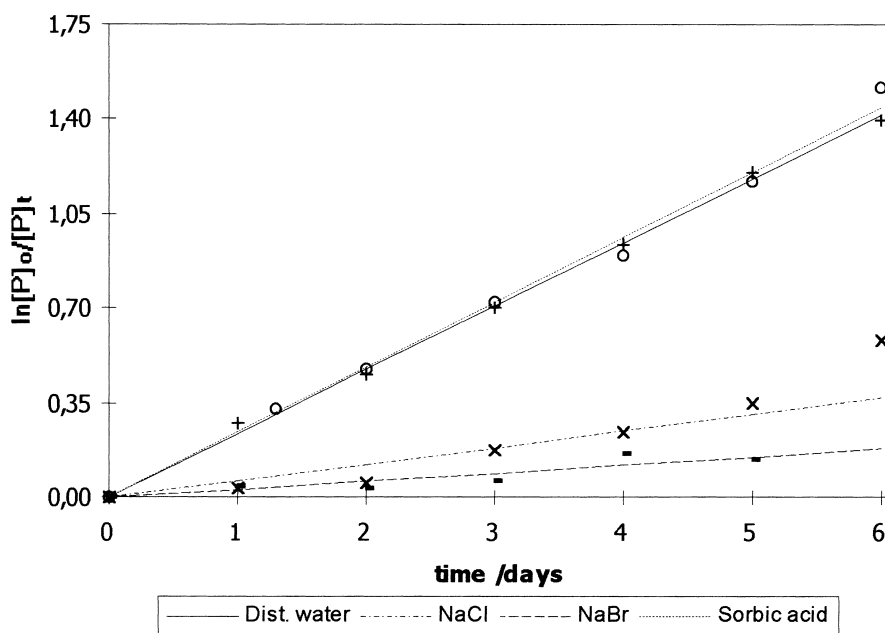


Fig. 3. Comparative study of fenarimol solar photodegradation in distilled water and different salt solutions with potential singlet and triplet state quenchers.

et al., 1970; Watkins, 1974; Shizuka *et al.*, 1980; Najbar and Mac, 1991; Najbar *et al.*, 1993) or an external heavy atom effect (Linschitz and Pekkarinen, 1960; Patterson and Rzed, 1975; Amorim *et al.*, 1977; Koziar and Cowan, 1978). To test the possibility that quenching involves an electron transfer mechanism the logarithm of the

quenching constants were plotted against the reduction potential (Stanbury, 1989) of the anions ($X^{\cdot-}/X^-$) (Fig. 5). For chloride, bromide and iodide the expected linear dependence was observed, supporting such a mechanism. The fact that SCN^- is slightly off this line may be a result of some specific interaction with the solvent. Heavy atom effects

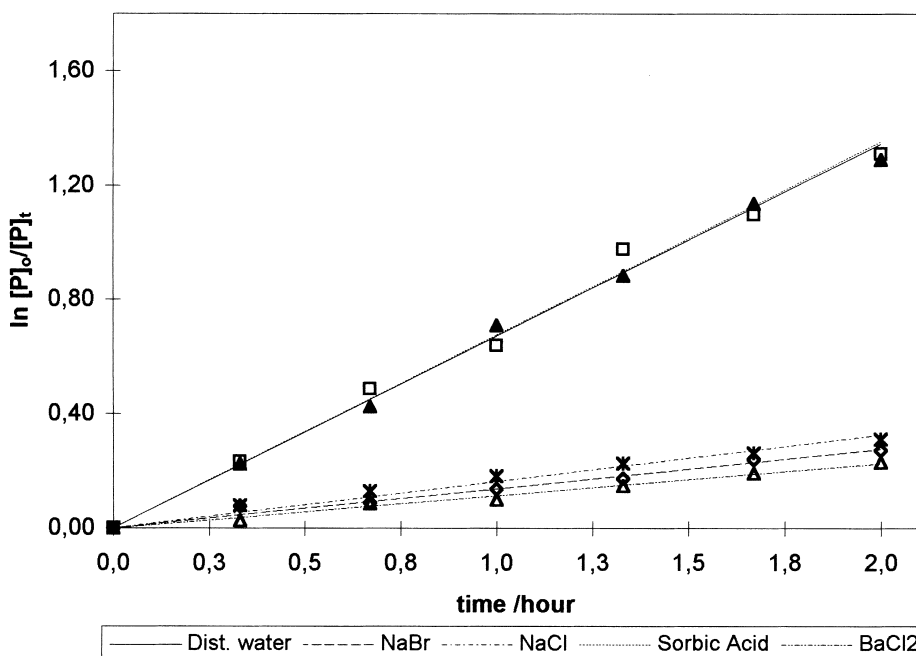


Fig. 4. Comparative study of fenarimol photodegradation in a photoreactor (313 nm) in distilled water and different solutions containing potential singlet and triplet state quenchers.

Table 3. Solar photodegradation rate of fenarimol in various solutions

Fenarimol solutions	k_{dp} (days ⁻¹)		$\phi_{rel.}^a$
	winter (cloudy sky)	winter (clean sky)	
Distilled water	0.13 ± 0.01 (pH 7)	0.24 ± 0.01	1
Sorbic ac. 1 mM pH7	0.13 ± 0.01		≈ 1
NaCl 0.5 M		0.061 ± 0.010	≈ 0.25
NaBr 0.5 M		0.030 ± 0.010	≈ 0.13

^aRelative quantum yield compared with distilled water.

Table 4. Photoreactor photodegradation rate of fenarimol, in various solutions

Fenarimol solutions	k_{dp} (h ⁻¹)	$\phi_{rel.}^a$
Distilled water (pH 7)	0.67 ± 0.03	1
Distilled water deaerated	0.64 ± 0.02	≈ 1
Sorbic ac. (1 mM, pH7)	0.68 ± 0.04	≈ 1
NaCl (0.5 M)	0.16 ± 0.02	≈ 0.23
NaBr (0.5 M)	0.13 ± 0.01	≈ 0.19
ZnSO ₄ (0.5 M)	0.72 ± 0.04	≈ 1
ZnCl ₂ (0.5 M)	0.16 ± 0.02	≈ 0.23
BaCl ₂ (0.5 M)	0.11 ± 0.01	≈ 0.16

^aRelative quantum yield compared with distilled water.

Table 5. Calculated ΔG values for quenching of fenarimol singlet state by halide ions

Electron donor ion	$E(X^-/X^-)$ ^a (V — vs SHE)	ΔG (eV)
Cl ⁻	2.41	-0.62
Br ⁻	1.92	-1.1
SCN ⁻	1.63	-1.4
I ⁻	1.33	-1.7

^aFrom: Stanbury (1989).

arise from increased spin-orbit coupling, and if this is involved the rate should depend upon the atomic number of the quencher (McGlynn *et al.*, 1969). The fact that chloride and bromide, which have higher atomic numbers than sulfur, are poorer quenchers than SCN⁻ suggests this effect is not important with these anions.

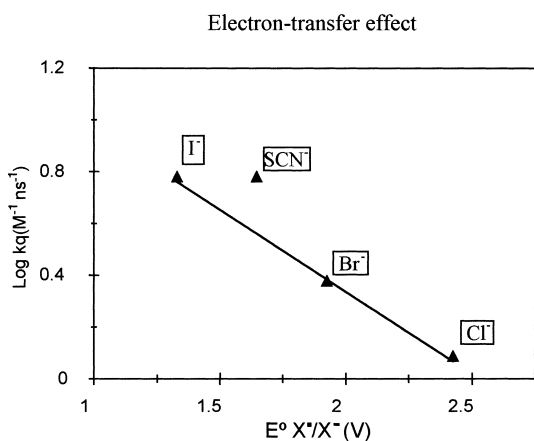


Fig. 5. Correlation between quenching constant and the reduction potential of the quenching ion X⁻ ($E_{(X^-/X^-)}$).

Various theoretical models have been used to interpret electron-transfer quenching of excited states (Marcus, 1960; Rehm and Weller, 1970; Formosinho and Arnaut, 1994). All of these relate the rate to the overall free energy change, but differ in terms of the relative importance of intramolecular structural changes and solvent reorganisation on the electron transfer. An excellent discussion of these differences has recently been presented (Formosinho and Arnaut, 1994). In the absence of detailed structural data on fenarimol, we have used the empirical Rehm–Weller approach (Rehm and Weller, 1970). If we take the potential energy variation between ground state and the 1st excited state of the fungicide:

$$\Delta E = E_{X^-/X^-}^{ox} + E_{A^+/A^-}^{red} + E_{S_1}$$

where E_{X^-/X^-}^{ox} = Oxidation potential of the tested inorganic ion in the ground state, E_{A^+/A^-}^{red} = Reduction potential of the aromatic compound in the ground state, E_{S_1} = Transition energy of the aromatic compound to the excited state S₁, and assume that $\Delta G = -nF\Delta E$ (using energy values in eV) we find that the free energy variation corresponding to charge transfer complex formation will be given by the Rehm–Weller approximation:

$$\Delta G = -E_{X^-/X}^{\text{ox}} - E_{A^+/A}^{\text{red}} - E_{S_1}$$

A half-wave reduction potential for fenarimol of -0.86 V (vs SHE) was determined. Using this, a fenarimol S_1 transition energy of 3.89 eV (obtained from the fluorescence spectrum) and literature values for halide reduction potentials, the reaction free energy (ΔG) was calculated for the different systems (Table 5). The calculated ΔG values are all negative (< -0.2 eV) and the quenching constants show the expected increase as the process becomes more exothermic (Rehm and Weller, 1970; Najbar and Mac, 1991; Najbar *et al.*, 1993), suggesting that the quenching mechanism by halide ions involves predominantly an electron transfer process. The lack of overall photoreduction of fenarimol on photolysis in the presence of these anions can be explained by this process being followed by back electron transfer, as has been suggested in the quenching of aromatic hydrocarbons (Najbar *et al.*, 1993).

Indications that a common mechanism is involved in the effects of salts on the photodegradation, comes from the fact that the ratio of reciprocal quantum yields for solar photolysis in the presence of NaBr and NaCl is identical to the ratio of their respective Stern–Volmer constants.

$$\frac{1/\phi_{\text{NaBr}}}{1/\phi_{\text{NaCl}}} = 2.03 \quad \frac{K_{\text{SV}}^{\text{Br}^-}}{K_{\text{SV}}^{\text{Cl}^-}} = 2.06$$

Observation of the fluorescence quenching rate constants for chlorides of different cations shows that an additional mechanism must also be involved with cesium(I), strontium(II) and barium(II). Since these cations do not have any other readily available oxidation state, quenching probably involves heavy atom effect, as has previously been suggested (Patterson and Rzad, 1975; Amorim *et al.*, 1977).

CONCLUSIONS

The observation that the photodegradation quantum yield of fenarimol decreases in the presence of singlet quenching salts (NaCl, NaBr, BaCl₂, ZnCl₂) and is not affected in the presence of O₂ or typically triplet quenching agents as sorbic acid, strongly supports the previous suggestion (Mateus *et al.*, 1994) that the excited state responsible for fenarimol photolysis under solar irradiation is the first singlet excited state, which has been shown (Mateus *et al.*, 1997) to have (n,π*) character.

Comparison of the quenching effects of halide ions on photolysis and fluorescence indicate a common mechanism, and the study of fluorescence quenching constants as a function of reduction potential of the anions suggest that this occurs by an electron transfer mechanism. This quenching effect

may be of practical use in photostabilisation of fenarimol in commercial formulations.

REFERENCES

- Amorim A. M. P. C., Burrows H. D., Formosinho S. J. and Silva A. M. (1977) The use of barium (II) to promote triplet ← singlet transitions in organic compounds: an external heavy-atom effect. *Spectrochim. Acta A* **33**, 245–246.
- Beer R., Davis K. M. C. and Hodgson R. (1970) Formation of excited charge-transfer complexes in the quenching of anthracene fluorescence by anions. *J. Chem. Soc. Chem. Comm.* 840–841.
- Dulin D. and Mill T. (1982) Development and evaluation of sunlight actinometers. *Environ. Sci. Technol.* **16**, 815–820.
- Evans D. F. (1960) Magnetic perturbation of singlet–triplet transitions. Part IV. Unsaturated compounds. *J. Chem. Soc.* 1735–1745.
- Formosinho S. J. and Arnaut L. G. (1994) Some new perspectives on electron transfer reactions through the intersecting-state model. *J. Photochem. Photobiol. A Chem.* **82**, 11–29.
- Koziar J. C. and Cowan D. O. (1978) Photochemical heavy-atom effects. *Acc. Chem. Res.* **11**, 334–341.
- Leifer A. (1988) *The Kinetics of Environmental Aquatic Photochemistry*. ACS Professional Reference Book, USA (Chap. 10).
- Linschitz H. and Pekkarinen L. (1960) The quenching of triplet states of anthracene and porphyrins by heavy metal ions. *J. Am. Chem. Soc.* **82**, 2411–2416.
- Marcus R. A. (1960) Exchange reactions and electron transfer reactions including isotopic exchange. *Discussions Faraday Soc.* **29**, 21–31.
- Mateus M. C. D. A., Silva A. M. and Burrows H. D. (1994) Environmental and laboratory studies of the photodegradation of the pesticide fenarimol. *J. Photochem. Photobiol. A Chem.* **80**, 409–416.
- Mateus M. C. D. A., Silva A. M. and Burrows H. D. (1997) UV-visible absorption spectra and luminescence of the pesticide fenarimol. *Spectrochim. Acta A* **53**, 2679–2684.
- McGlynn S. P., Azumi T. and Kinoshita M. (1969) *Molecular Spectroscopy of the Triplet State*. Prentice-Hall, Englewood Cliffs.
- Morris D. F. C., Short E. L. and Waters D. N. (1963) Zinc Chloride and Zinc Bromide complexes. III. Structures of species in solution. *J. Inorg. Nucl. Chem.* **25**, 975–983.
- Najbar J. and Mac M. (1991) Mechanisms of fluorescence quenching of aromatic molecules by potassium iodide and potassium bromide in methanol–ethanol solutions. *J. Chem. Soc. Faraday Trans.* **87**, 1523–1529.
- Najbar J., Wirz J. and Mac M. (1993) Transient radicals formed by electron transfer between inorganic ions and excited aromatic molecules in polar solvents. *Helv. Chim. Acta* **76**, 1319–1331.
- Patterson L. and Rzad S. J. (1975) Quenching of aromatic hydrocarbon fluorescence by Cesium Chloride. *Chem. Phys. Lett.* **31**, 254–256.
- Rehm D. and Weller A. (1970) Kinetics of fluorescence quenching by electron and H-atom transfer. *Israel J. Chem.* **8**, 259–271.
- Righellato E. C. and Davies C. W. (1930) The extent of dissociation of salts in water. Part II. Uni-bivalent salts. *Trans. Faraday Soc.* **26**, 592–600.
- Shizuka H., Nakamura M. and Morita T. (1980) Anion-induced fluorescence quenching of aromatic molecules. *J. Phys. Chem.* **84**, 989–994.
- Short E. L. and Morris D. C. (1961) Zinc Chloride and

- Zinc Bromide complexes. I. *J. Inorg. Nucl. Chem.* **18**, 192–198.
- Stanbury D. M. (1989) Reduction potentials involving inorganic free radical in aqueous solution. *Adv. Inorg. Chem.* **33**, 69–138.
- Watkins A. R. (1974) Short-lived intermediates formed by the interaction between electronically excited molecules and inorganic ions. *J. Phys. Chem.* **78**, 2555–2558.
- Worthing C. R. (1983) *The Pesticide Manual*, 7. British Crop Protection Council, London.