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Decomposition of a phthalocyanine dye in various conditions under UV or visible light irradiation

Tullio Caronna [*], Claudio Colleoni, Stefano Dotti, Francesca Fontana, Giuseppe Rosace

Dipartimento di Ingegneria Industriale, Facoltà di Ingegneria, Università di Bergamo, Viale Marconi 5, I-24044 Dalmine, Bergamo, Italy

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Abstract

The photostability of a copper complex of a phthalocyanine dye at 313 nm and under visible light was investigated in various solvents both in the presence or absence of O_2. The dye was found relatively stable in water, while substantial decomposition, in different times, occurs in methanol, ethanol, acetone and dimethylformamide. A study of the products formed in some of these solvents was performed, allowing to elucidate the mechanism of the colour fading. An interesting and unexpected effect was found in the case of mixed solvents. The presence of acetone in the hydroxylated solvents, even at very low concentration, increases dramatically the rate of decomposition of the dye. This effect is strongly enhanced with increasing of the aliphatic chain size of the ketone. A hypothesis on this effect is put forward.

Keywords: Phthalocyanine dye; Singlet oxygen; Photostability; Mixed solvent

1. Introduction

Phthalocyanines have been subjected to intensive studies since the time of their synthesis for the particular properties deriving from their extended π-system. Furthermore, the presence of four conveniently located nitrogen atoms allows the formation of a series of complexes with metal ions and actually, in the majority of their applications, these molecules are used in the form of metal complexes. Depending on the choice of the metal ion, these complexes may be used for applications ranging from conventional dyestuffs to catalysis, from coatings for read/write CD-ROMs to an anti-cancer agent [1,2]. Nowadays their use as dyestuffs is increasing, both because of colour fastness [3] on the fabric, and for the possibility of subsequent wastewater treatment [4].

In recent times, phthalocyanine complexes with zinc, lead, magnesium, etc. have been studied [5,6], evidencing the importance of the solvent and the wavelength used for the degradation; the formation of singlet oxygen as a deactivation path of the excited state was observed as well, but some of the studies regarding degradation of these complexes were run in solvents (DMF, DMSO and pyridine) that are not used normally in industrial dyeing, and the irradiation was carried both in the ultraviolet [5] and the visible range [7].

Because one of these dyes (Direct Blue 199, number 74190 in the Colour Index) (Fig. 1), actually in use, is a copper complex of some phthalocyanine derivatives, and considering that, to the best of our knowledge, no studies on these complexes have been reported so far, we decided to start an investigation on the stability of this complex in the UV region as well as under visible light in a certain number of solvents with the final idea to develop a method that may eventually be used for the treatment of the wastewater.

2. Materials and methods

All chemicals are commercial products. Phthalocyanine (PH) was a generous gift of the chemical company CHT, Italy. It was purified, according to commonly applied methods, in the following way: 20 mg of PH was dissolved in 50 mL of DMF, then hexane was added to the blue solution until the dye precipitated as a blue powder in almost quantitative yield.

Irradiations were performed in a Helios Italquartz photochemical reactor equipped with 10 lamps irradiating at 313 nm or at 400–700 nm, in Pyrex reactors. The temperature in the irradiation chamber was thermostated at 293 K.

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[*] Corresponding author. Tel.: +39 035 2052322; fax: +39 035 562779.
E-mail address: tullio.caronna@unibg.it (T. Caronna).

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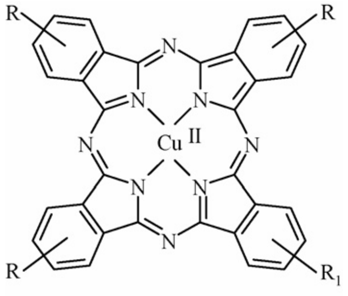


$R = SO_2NH_2$ $R_1 = SO_3NH_4$

Fig. 1. Direct Blue 199, number 74190 in the Colour Index.

The ultraviolet–visible absorption spectra were recorded on a Thermo Nicolet Evolution UV–vis-500 spectrophotometer, Vision 32 software using a 1 cm pathlength cell. The ATR FT-IR spectra were recorded on a Thermo Avatar 370. All the spectra were recorded at room temperature.

Solutions were prepared in the following solvents: water, methanol, ethanol, acetone, DMF. The concentration of PH was adjusted around 10^{-5} M in order to obtain absorbance values ranging between 0.3 and 0.4.

All the solutions used in the photochemical experiments were irradiated both under aerated and deoxygenated conditions. In this last case, the solutions were deoxygenated bubbling dry nitrogen for 30 min.

To determine the photolysis decomposition products, solutions of PH were irradiated until complete decolourisation of the solution, confirmed by absorbance measurements, in the following solvents: water, methanol, ethanol, acetone, DMF.

Thereafter, the solvent was evacuated and ATR FT-IR spectra were run on the residue.

The use of mixed solvents was also studied adding 0.1% of DMF, acetone, ethanol, methanol to water or methanol solutions.

In the case of the addition of acetone, decolourisation was strongly accelerated, while in all other cases no variations were observed. The effect of acetone concentration was studied by preparing two 10^{-3} M solutions of PH, one in water or alcohol (MeOH or EtOH) and the other in acetone or other ketones (butan-2-one, pentan-3-one and 2,4-dimethylpentan-2-one). Kinetics were then run by mixing selected volumes of the water solution and of a solvent, as illustrated in Table 1, for the mixtures water:acetone, adding either the first or the second solvent up to the volume of 100 mL, in order to realize the correct solvents ratio with a final concentration of 10^{-5} M and taking out the 20 mL used to run the experiments.

Table 1
Volumes of PH solutions in acetone, water and solvent used to run the kinetic experiments in mixed solvents

Acetone (mL)	10^{-3} M PH in water (mL)	Solvent (mL)	Solvents ratio (v/v)
0	1	Water (99)	0:100
10	1	Water (89)	10:90
30	1	Water (69)	30:70
50	1	Water (49)	50:50
70	1	Water (29)	70:30
90	1	Water (9)	90:10
10^{-3} M PH in acetone	0	Acetone (99)	100:0

When the same study was conducted irradiating with visible light, only 0.1% of ketone was used, and the solutions were realized by directly adding the ketone to a mother solution of the dye.

3. Results and discussion

Fig. 2 reports the rate of bleaching of the dye in water, MeOH, EtOH, acetone and DMF when irradiated at 313 nm. The choice of these solvents was limited by dye solubility. The figure shows strong dependence of the rate on the nature of the solvent, the colour fading being much faster in DMF than in the other solvents. For comparison, the rates of decomposition at 313 nm and under visible light are reported in Table 2. The slowing down of the decomposition at longer wavelength is evident, while the trend in the decomposition is maintained.

In the following discussion, we do not distinguish between the two wavelengths, the rate of decomposition being the only difference, while all other considerations apply to both cases.

In Fig. 3 the rate of disappearance of PH in aerated or degassed water is reported. The same trend was found also for the other solvents reported in the present study. The great enhancement of the rate of disappearance in degassed solvents clearly indicated that oxygen plays a role in the deactivation of the excited state of the dye. It was already reported in literature that phthalocyanines, either free or complexed with different metal ions [8–10], generate singlet oxygen that may either decay

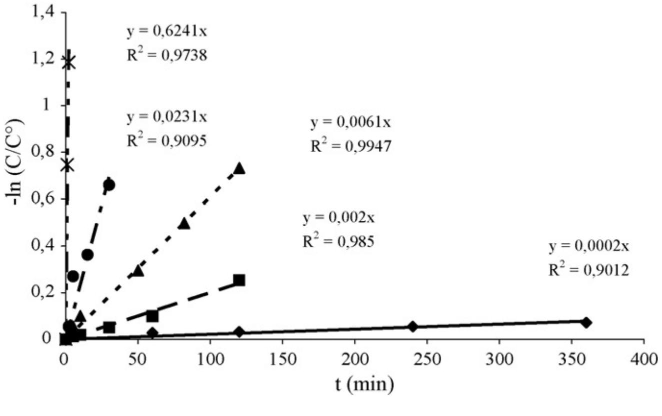


Fig. 2. Rate of disappearance of PH in water (♦), MeOH (■), EtOH (▲), acetone (●), DMF (×).

Table 2
$\ln(C^0/C)/t$ (in s^{-1}) of the PH dye in different solvent at 313 nm and visible light

Solvent	313 nm	Visible
Water	0.0002	0.0001
Methanol	0.0020	0.0002
Ethanol	0.0061	0.0027
Acetone	0.0231	0.0068
DMF	0.6241	0.0091

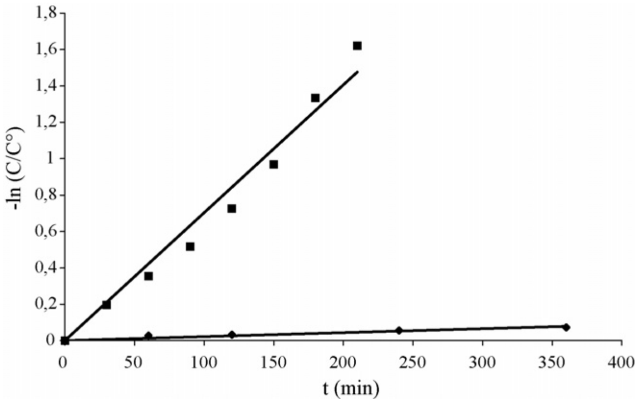


Fig. 3. Disappearance of PH in degassed (■) or aerated (♦) solutions.

Table 3
Lifetime of singlet oxygen in the used solvent and relative references

Solvent	Lifetime (μs)	Reference
Water	4	[11a]
Methanol	11	[11b]
Ethanol	13	[11c]
Acetone	54	[11d]
DMF	19	[11d]

or eventually attack the phthalocyanine, forming phthalimide derivatives.

While, on one side, there is an obvious effect of oxygen and the different rate of dye degradation may be due to singlet oxygen lifetime, on the other side the solvent itself may be taken into consideration for several reasons illustrated below. In the literature [11] the dependence of the lifetime of singlet oxygen from the solvent is reported: in Table 3 are given the values for the solvents we used.

A plot of the singlet oxygen lifetime against the rate of disappearance of the dye (Fig. 4) shows that four solvents correlate fairly well, while DMF is badly out of the line. Therefore, a first hypothesis may be that the longer the singlet oxygen lifetime, the higher is the chance that this species attacks the dye. Following this reasoning, one may suggest that the rate of decolourisation in DMF could follow a different mechanism.

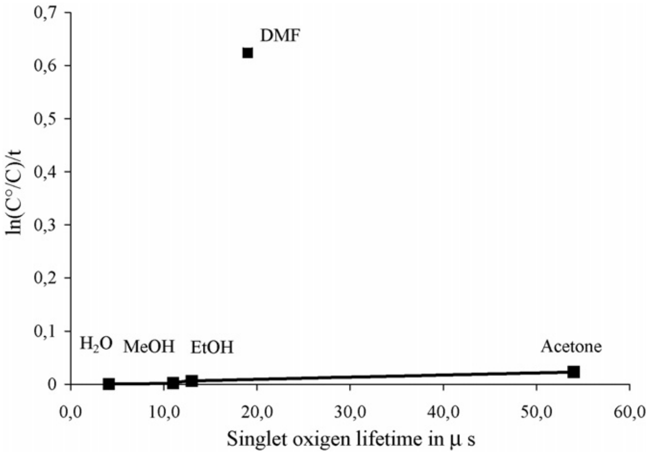


Fig. 4. Singlet oxygen lifetime vs. rate of disappearance of PH in water, MeOH, EtOH, acetone, DMF.

From another point of view, some solvents may give rise to the formation of radicals, arising from the solvent itself, affecting the reaction pathway. An important clue came from comparison of the IR spectra of the products obtained in aerated and degassed solution (Fig. 5).

If the reaction in aerated solution proceeds through attack of singlet oxygen onto PH, the product(s) obtained in this case obviously could not be obtained in degassed solution. Actually, IR spectra obtained in aerated or degassed acetone, methanol or ethanol are identical. In all cases, IR spectra of the crude, completely decolourised reaction mixture were run after thorough evaporation of the solvent (Fig. 5b–e) and compared with the IR spectrum of PH (Fig. 5a). The band around 1130 cm^{-1} is present in all the IR spectra in Fig. 5 and may be attributed to the sulfonic group. The spectra of the products for the reactions run in acetone showed a strong band at 1707 cm^{-1} that can be attributed to stretching of the C=O (Fig. 5b), while those for the reactions run in methanol showed the presence of a strong band at 3354 cm^{-1} (O–H stretching) and a smaller band at 2923 cm^{-1} (C–H aliphatic stretching) that may be explained with addition of a methylol group onto the PH molecule (Fig. 5c); the reaction in ethanol yields products showing analogous O–H and C–H stretching bands at 3366, 2922 and 2852 cm^{-1}, suggesting CH_3–CH–OH group addition (Fig. 5d). For the reaction run in DMF a highly viscous oil was obtained after evacuation of the solvent. This oil was treated with acetonitrile to obtain a yellow solid that was separated via filtration, and the IR spectrum showed a pattern of absorbance different from those of the other solvents, showing a band at 1656 cm^{-1} compatible with the expected presence of an amido group (Fig. 5e).

The reactions in water were not examined because of the exceedingly slow rate of decolourisation. These findings suggest that some radicals, generated from the solvent, attack the dye breaking the π-system and giving rise to decolourisation. As far as we know, no reactions are reported between singlet oxygen and acetone, which rules out the possibility that the radicals may be created through this way. Another possibility is electron transfer from the solvent to the excited state of PH. A possible mechanism involving methanol is depicted in Scheme 1.

We cannot exclude that in some cases there is formation of substituted phthalimide or of some kind of broken or open phthalocyanine or else, but obviously it depends from the ease of formation of other radicals from the solvent compared with the oxidation reactions.

An interesting result was obtained with the use of mixed solvents. While in mixtures between water and the alcohols no particular effect was found, an increase in the rate of dye decomposition was found when acetone was mixed with the other solvents. This finding prompted us to start a study regarding how different water (or MeOH or EtOH):acetone ratios may affect the rate of decomposition of our phthalocyanine. In Fig. 6 the rate of disappearance versus percentage of acetone in the solvent mixtures is reported.

In the literature a certain number of data concerning singlet oxygen lifetime in mixed solvents are reported, showing how

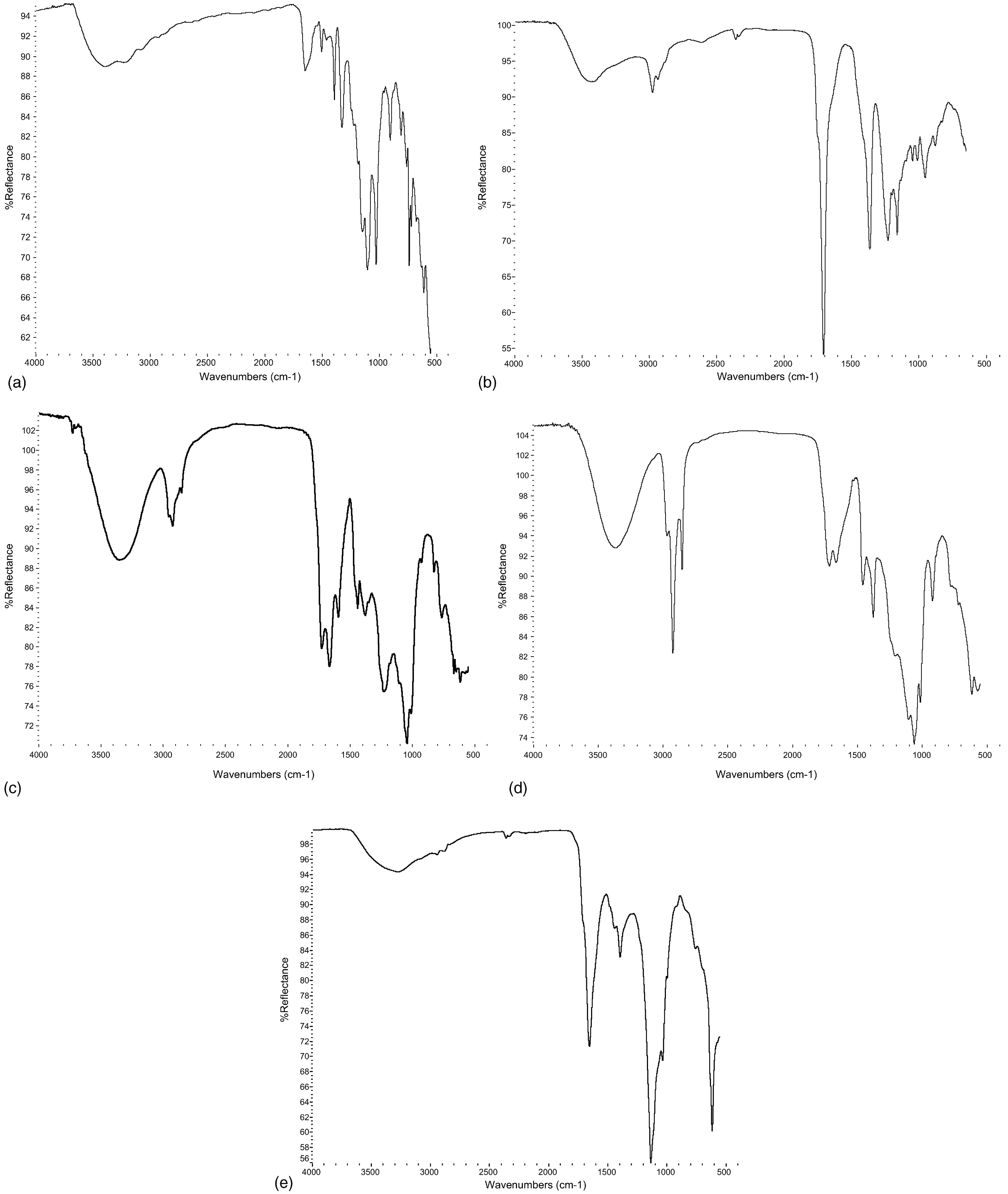
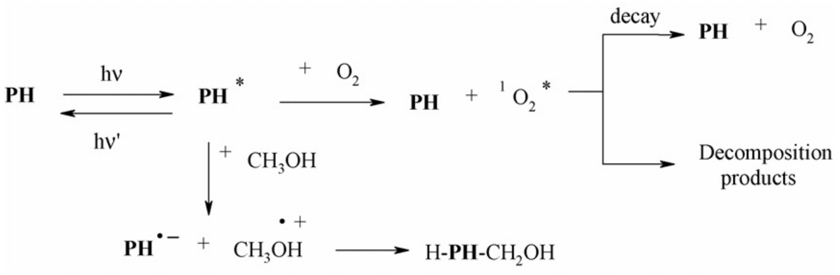


Fig. 5. IR spectra for: (a) the phthalocyanine; the decomposition product(s): (b) in acetone, (c) in methanol, (d) in ethanol (the spectra b–d are the same both for the aerated and the degassed solution), (e) in DMF (aerated solution).



Scheme 1.

addition of even small amounts of hydroxylated compounds to a non-hydroxylated one always shortens its lifetime (e.g. 0.03 s in CCl_4 and 3.1×10^{-4} s in CCl_4:MeOH 98:2) [11e]. Unfortunately, as far as we know, no data concerning ketone–alcohol mixtures have been reported; we think, however, that we may safely assume this behaviour to occur also in solvent mixtures containing acetone. In our case, working either at 313 nm or under visible light, even the addition of small amounts of water, MeOH or EtOH to the acetone solution increases instead the rate of dye bleaching, indicating that this effect cannot be ascribed to the lifetime of excited oxygen. We may anticipate that the same effect was found at both wavelengths even if there are some differences in the rate of decomposition. Interestingly, a maximum in the rate of dye bleaching is always reached when the amount of acetone in the mixture ranges around 10%. A somewhat similar behaviour was reported for the bleaching of dyes in micelles [12]; the author justified this behaviour as due to the swelling of micelles at low concentration of the hydroxylated solvent, and to their decomposition at higher concentration. In a later paper the same effect was found when phthalocyanines are enclosed in SiO_2 gel [13]. Since neither micelles nor gels are present in our system, and despite the fact that, under our irradiation conditions, acetone cannot be excited, we may consider the presence of the ketone as responsible for the dye degradation. For this reason, other aliphatic ketones, namely butan-2-one, pentan-3-one, and 2,4-dimethylpentan-2-one, whose structures are closely related to acetone, were used instead. As is reported in Table 4, not only all these ketones increased the rate of degradation both in water and in MeOH, but the disappearance of the dye becomes even faster by increasing the chain size from acetone to 2,4-dimethylpentan-2-one.

Table 4
$\ln(C^0/C)/t$ (in s^{-1}) of the PH dye in solution of mixture of water (or MeOH):ketone 99.9:0.1 (v/v)

	Water (313 nm)	Water (visible)	MeOH (313 nm)
Acetone	0.25	0.0003	0.017
Butan-2-one	4.24	0.0027	0.092
Pentan-3-one	6.30	0.0068	0.200
2,4-Dimethylpentan-2-one	–	–	1.000

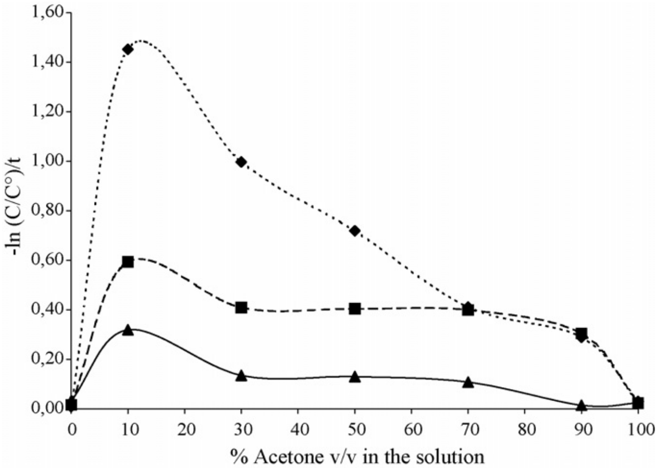


Fig. 6. Acetone (%, v/v) in the solution vs. rate of disappearance of PH in water (♦), MeOH (■), EtOH (▲).

The same behaviour was also found working under visible light, even if reaction rates were lower compared to those at 313 nm. A deeper study of these effects is beyond the scope of the present work, yet some considerations may be done. There is a strong acceleration due to the presence of a certain amount of ketone and depending on the aliphatic chain of the ketone. Since we only used aliphatic ketones, whose chemical and photochemical behaviour is similar, we think we can rule out the involvement of excited ketones or radicals arising from the ketones. The fact that the rate of degradation increases by increasing the length and the complexity of the aliphatic substituent should be related to the insertion of the ketone in the solvent coordination sphere, either in the fundamental or in the excited state; this would destabilize the dye allowing its faster reaction. This effect will be further investigated in the next future.

4. Conclusions

The study showed that phthalocyanine dyes have different mechanisms of degradation depending on the solvent and the amount of oxygen dissolved therein. Addition of acetone or other aliphatic ketones to the reaction solvent accelerates in all cases the bleaching of the dye. These results give interesting hints to possible treatments of wastewater from dyeing processes.

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