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Short communication

Fading modelling of a hair oxidation dye: aminoindamine

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Abstract

Aminoindamine and aminoindoaniline transformation on hair, faster under vacuum than in the presence of oxygen, produces two colourless photoproducts in each case. To facilitate and accelerate the study, modelling of this transformation in solution and on film is carried out. Degassed aqueous solution containing amino acids and poly(vinyl alcohol) films seem to be the good systems to study dyes transformation on hair. Validity of the system is checked by the obtention of the same transformation products as on hair; structural elements are identified by IR spectroscopy and their structure confirmed by NMR and mass spectroscopies.

Keywords: Oxidation dye; Photochemical and thermal degradation; Aminoindamine; Modelling; Poly(vinyl alcohol); Gelatin; Keratin; Amino acids

1. Introduction

Covering grey hair today means both seduction and fashion. The most suitable kind of colouration is oxidation dyeing [1–10] which offers a great variety of shades, which are more or less fast.

Three major categories of hair colouration can be indexed and classed as temporary, semi-permanent and permanent hair dyes. Whereas temporary colourants are removed by single shampoo, semi-permanent ones remain for 4–6 weeks. Permanent dyeing process is different from the first two processes: small and colourless or light coloured precursors [11] are deposited on hair; after migrating into the hair, they react to form a larger molecule. Thus the dye is confined in the fibre for a long time. For example, aminoindamine (blue) and aminoindoaniline (red) are synthesised on hair from two precursors namely base and coupler. The blue colour results from the coupling of paraphenylenediamine (PPD) and 2-diamino-2,4-phenoxyethanol (DAP), and the red colour from paraaminophenol (PAP) and the same coupler DAP. Corbett explains in several papers the detailed mechanism of hair colouring [3,10,12–21].

Determining hair dye transformation is nowadays a major challenge for the cosmetic firms. In a previous paper [22], fading of aminoindamine and aminoindoaniline on hair was examined. In both the cases, two main colourless photoproducts were obtained. Considering that dyed hair transformation was slower in the presence of oxygen than in the presence of nitrogen, and considering the absence of photoproducts after irradiation in oxygen bubbled water, we concluded that oxygen inhibited hair dyes transformation. Moreover, irradiation of an indamine solution in nitrogen bubbled isopropanol led to the same photoproducts as on hair. This last experiment confirmed that the reaction involved a photoreduction step. The contribution of hair to the transformation mechanism was also observed. None of the colourless photoproducts were formed from solid indamine or aqueous solution of dye even in oxygenless conditions.

An ageing study on hair dyes is time consuming. Moreover, the dyeing process on hair requires strict experimental conditions—homogeneous irradiation of hair being rather difficult—and the study of any chemical modification in hair should often involve an extraction technique. The modelling of such a complex system would bring a new insight if such a possibility would exist. We therefore investigated the replacement of hair by some solid organic models easier to handle, expose and analyse. Simultaneously, we tried to reproduce in solution the phototransformation observed in dyed hair. The first solid material selected as hair model was gelatin, a parent proteinic macromolecule. Gelatin transparency in the visible range was high enough to follow dye transformation after irradiation of hair dyes by UV–visible spectroscopy. Post-irradiation analysis was performed using HPLC after dissolution in neutral water.

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The second solid material selected was PVA (poly(vinyl alcohol)), a polymer known for its low oxygen permeability and its reducing properties, two parameters favouring photoreduction. PVA containing hair dye was also easily irradiated and subsequent analysis was carried out either in the solid state using FT-IR and UV–visible spectroscopies or after dissolution in aqueous solution using HPLC.

In our previous paper, we pointed out that dye transformation on hair was probably a reduction. In order to model the transformation in solution, products which could reduce the dye were added to an aqueous solution of indamine. Hair contains cystine, tryptophan, histidine, respectively, at a ratio of 14:1.1:0.8% [1]. Cystine is present in hair as keratocystine. Considered as good reducers, these amino acids could explain the strong hair-reducing characteristics. When diluted iodine is placed in the presence of hair, iodine is indeed reduced [1]. Moreover, amino acids such as tryptophan and histidine effects are reported in different studies on textiles [25]. Thus, these amino acids are probably involved in the process of dye transformation and would be a good model of hair dyes fading. It was decided to use the "L" natural isomer amino acids.

As handling solutions is obviously easier than films and as they can be directly used in liquid chromatography, identification was performed using solutions; MS and NMR analyses were carried out to confirm that the transformation products were the same as those obtained on hair.

2. Material and methods

2.1. Chemicals and materials

O-phosphoric acid 85% Normapur, PVA Rhodoviol 4/125 and gelatin were provided by Prolabo. CLHP acetonitrile was provided by Carlo Erba (>99.8%). Heptane sulphonic acid monohydrate was provided by Janssen Chimica (>98%). Amino acids: L-histidine, L-tryptophan and L-cystine (>98%) were provided by Prolabo, and L-cysteine (>97%) and ammonium acetate (>98%) by Aldrich.

2.2. Film making and dyeing

Three types of gelatin films were elaborated: a neutral one and two others with keratins of two different molecular weights. Compositions are indicated in Table 1.

Table 1
Composition of gelatin films

	Gelatin film (g)	Gelatin film with keratin A (g)	Gelatin film with keratin B (g)
Gelatin	5.0	5.0	7.5
Keratin A hydrolysate	–	5.0	–
Keratin B hydrolysate	–		10.0
30% Aqueous formol	1.0	1.0	1.0
Water qsp	100	100	100

Gelatin and keratin were dissolved into 70 g of stirred water at 60 °C. Then, formaldehyde was added to the solution as a cross-linking agent. After a quick stirring, 20 g of the mixture were poured in Petri dish and evaporated until films dry at room temperature.

Permanent dyeing process was carried out on gelatin films like on hair with the S dyeing solution:

Base: PPD (for blue dye) or PAP (for red one)	3×10^{-2} M
Coupler (DAP)	3×10^{-2} M
20% Ammonia solution	10.7 M, 20 ml
Water qsp	100 ml

Twenty grams of an equal amount of H_2O_2 cream (20 volumes) added to the S dyeing solution was needed for the colouration.

To make PVA films, 1 g of PVA was dissolved in 10 ml water at 50–60 °C. The mixture was quickly poured in a Petri dish and dried at room temperature after stirring. For dyed PVA films, the aminoindamine dye was introduced during the film elaboration. Films containing two different concentrations of the dye were prepared (see Table 2).

Dye was slightly dissolved in methanol. Simultaneously, 1 g of PVA was dissolved in 10 ml water at 50–60 °C. Dye solution was incorporated into the PVA solution and mixed together. The dyed mixture was rapidly poured in a Petri dish and dried at room temperature.

2.3. Apparatus

2.3.1. Irradiation apparatus

Two types of irradiations were carried out:

1. Polychromatic irradiation centred at 310 nm using 6 Duke Sun Lamps (20 W) in a cylindrical reflector at 35 °C.
2. Polychromatic irradiation in an SEPAP 12/24-ATLAS at 60 °C. In this unit, the incident light contains only wavelengths longer than 300 nm. Irradiation is done in dry conditions by four MAZDA 400 W high pressure mercury sources filtered with a borosilicate envelope and located at the four corners of a square chamber [23].

2.3.2. Analysis

High-performance chromatography analyses were carried out with a WATERS 990 chromatograph fitted with a photodiode array detector. The SFCC C8 Ultrabase UB 135 column (5 μm × 150 mm × 4.6 mm) was used with a water/acetonitrile mixture. A GILSON 306 chromatograph equipped with a Hewlett Packard 1040 photodiode array detector and a SUPELCOSIL SUPLEX

Table 2
Composition of PVA dyed films

Spectroscopic method	UV–visible	IR
Indamine (g/film)	0.0006	0.0150

Pkb-100 (250 mm × 2.1 mm × 5 μm) column dealt with the semi-preparative separation. Peak detection was achieved at 240 nm in both the cases.

HPLC conditions:

- Blue dye (indamine): 85% A (0.050 M ammonium acetate buffer and 2.0×10^{-3} M sodium monohydrate 1-heptane sulphonic acid) and 15% B (acetonitrile); flow: 1 ml/min.
- Red dye (indoaniline): 83% A (pH 3, phosphoric acid in water and 2.0×10^{-3} M sodium monohydrate 1-heptane sulphonic acid) and 17% B (acetonitrile); flow: 1 ml/min.

IR spectra were carried out with an FT-IR Nicolet 20 SX and a 5 SX spectrophotometers. For solutions, UV–visible measurements were recorded by a Cary 13E spectrophotometer. For films, UV–visible measurements were obtained with a Lambda 5 Perkin Elmer spectrophotometer equipped with an integrating sphere. Dyes and photoproducts structures were determined by NMR spectroscopy using a BRUKER AC 400 spectrometer.

Mass spectra were provided by the CNRS (Lyon, France) using a device operating in a 70 eV scan mode.

3. Experimental results

3.1. Modelling of blue dye transformation on gelatin

Gelatin films were cross-linked by formaldehyde. Lambswool A and B keratin hydrolysates were added in some films, B having a higher molecular weight than A. Dyeing of these films was carried out with the same base and coupler as the pure gelatin: PPD + DAP for a blue dye and PAP + DAP for a red one.

After dissolution, gelatin film evolution was studied by two methods: liquid chromatography and UV–visible spectrophotometry at 513 nm corresponding to the maximum wavelength emission of the dye in film in the case of PPD + DAP (blue dye formed on hair).

Pure gelatin film chromatogram showed that gelatin peaks corresponded to high intensity peaks with retention times lower than 5 min. In the case of dyed film, colouration was not homogeneous. Gelatin film shades were the same as dyed hair ones. Following the chromatogram evolution as a function of the irradiation time, the disappearance of half of the dye within 2 h was noted. The dye peak and the first photoproduct peak (like B1 on hair) were observed, but the equivalent of B2 was not formed. B2 was not found in any conditions and even with longer irradiation.

The dyed gelatin films evolution was examined in the presence of A and B keratins. The gelatin films containing keratin faded faster than the pure one. Half of the dye was decomposed in 40 min. B1 was detected but not B2. In the same time, the study of film evolution by UV–visible spectroscopy confirmed the previous results obtained by liquid chromatography.

For PAP + DAP mixture, the same analyses (liquid chromatography, UV–visible spectroscopy at 478 nm—maximum wavelength of the dye in film) were performed. As for PPD + DAP results, only one (R1) of the two photoproducts obtained on hair was detected on gelatin films. The same results were obtained with dyed films elaborated with A or B keratin hydrolysates.

In conclusion, keratin had no effect on the dye photoreduction, and the second photoproduct was not observed under any conditions. Consequently, gelatin film is not a satisfying model.

3.2. Modelling of indamine transformation on PVA

PVA films were elaborated as explained in Section 2.2. Unlike the gelatin films, PVA films were dyed directly with indamine. For the case of UV–visible and IR spectroscopy analyses, two films were elaborated with different dye concentrations.

In the first step, as indamine UV–visible spectrum on PVA film differed from the spectrum of indamine in aqueous solution, degradation evolution versus irradiation time was followed at 600 nm, the maximum absorption wavelength of indamine in film (versus 513 nm in solution). After about 8 h irradiation in an SEPAP 12/24-ATLAS unit at 60 °C, the blue dye disappeared faster under vacuum than in the presence of oxygen, as on hair. In parallel it was observed that when the non-irradiated blue film spectrum is subtracted from the irradiated one, the appearance of a spectrum corresponding to the addition of B1 and B2 photoproducts spectra was observed.

In the second step, different films of PVA dyed with synthetic indamine were irradiated for about 208 h in an SEPAP 12/24-ATLAS. IR analyses of these films showed two broad peaks—probably the quinonic ones—at 1600 and 1545 cm^{-1} which diminished, while a peak appeared at 1520 cm^{-1} (see Fig. 1). This result could be explained by the quinone diimine aromatisation.

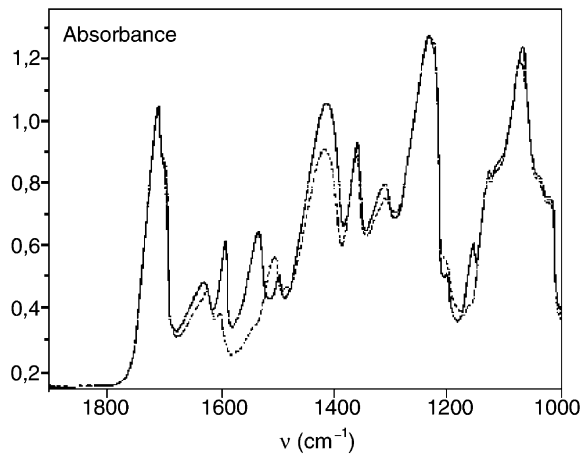


Fig. 1. IR spectroscopy: blue dyed PVA film evolution during irradiation in an SEPAP 12/24 chamber ((—), non-irradiated; (- - -), irradiated).

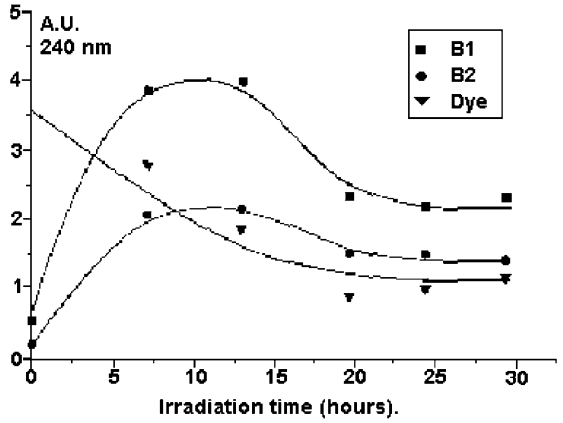


Fig. 2. Detection at 240 nm of indamine and its photoproducts during blue dyed hair irradiation in an SEPAP 12/24 chamber (extract injected in HPLC).

Using IR or UV spectroscopies, the blue dye disappearance was also faster under vacuum than in the presence of oxygen.

Since PVA is soluble in water, the solutions obtained from films analysed by IR and UV–visible spectroscopies were injected in HPLC. The presence of two photoproducts B1 and B2 was detected on the chromatogram. Photoproducts evolution versus irradiation time on PVA and hair are shown in Figs. 2 and 3.

To summarise, only one of the two photoproducts was obtained from gelatin films, whereas both photoproducts were formed with PVA films. The PVA film therefore appears to be a good model for blue hair dye study.

3.3. Modelling of indamine transformation in solution

The impact of L-histidine (1 g/l) on indamine transformation was examined next. L-histidine was introduced into a 2.0×10^{-4} M aqueous solution of indamine to obtain an amino acid concentration at least 10 times higher than the dye. This solution was irradiated for about 24 h under vacuum in an SEPAP 12/24 chamber as the transformation was accelerated in oxygenless conditions. Amino acid absorption at λ longer than 300 nm being negligible, the indamine transformation versus irradiation time at 513 nm (maximum wavelength absorption of the dye in solution) was observed. A slower transformation rate was noticed for the aqueous solution of indamine alone than in the presence of histidine. After about 24 h irradiation, 60% of the dye alone had disappeared compared to 93% of the dye in the presence of the amino acid. Thermal transformation at 60 °C was accelerated in the presence of L-histidine.

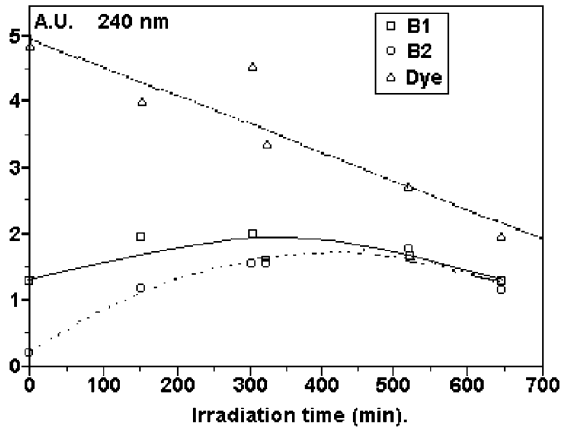


Fig. 3. Detection at 240 nm of indamine and its photoproducts during blue dyed hair irradiation in an SEPAP 12/24 chamber (extract injected in HPLC).

Secondly, the 60 °C thermal and photochemical transformations of the same degassed indamine aqueous solution containing amino acids such as tryptophan (1.0 g/l), cysteine (1.0 g/l) or cystine (0.5 g/l) was examined during 24 h (the low solubility of cystine in water explained the lower concentration used in solution). In the case of tryptophan and cystine, the formation of B1 was favoured instead of B2 for the cysteine. In the presence of cysteine, the B1 and B2 formation rates were higher than those of tryptophan and cystine. B1 and B2 formation was detected in all the cases. However, thermal transformation of the blue aqueous solution of indamine containing L-cystine under vacuum first led to a colourless solution. After a 30 min contact, the solution was analysed; neither B1 nor B2 products were detected. After a 30 min additional irradiation of this colourless solution at 60 °C, the formations of B1 and B2 products were finally observed.

In conclusion, the thermal or photochemical transformations under vacuum of an aqueous indamine solution in the presence of amino acids lead to the formation of the same products as those obtained during the blue dyed hair transformation. Moreover, discolouration seems to be an intermediate step during the photoproducts formation as for the diphenylamine formation. The photoproducts B1 and B2 are then formed in a subsequent step.

3.4. Identification of the transformation products

To identify the products obtained in an aqueous solution of indamine in the presence of amino acids and compare these results with those obtained on hair with PPD + DAP in a previous paper [22], a deoxygenated aqueous solution of indamine (2×10^{-4} M) and L-cystine (0.5 g/l) was irradiated for 12 h in an SEPAP 12/24 chamber. To isolate the photoproducts, 2-l of the irradiated solution were filtered, then injected 1.5 ml × 1.5 ml and eluted on a semi-preparative HPLC column. The buffer required in the first separation was removed by a second separation and the B1 and B2 photoproducts were isolated. Collected fractions were both analysed by liquid chromatography and spectrometry.

First, UV–visible absorption spectra of the isolated photoproducts were the same as those obtained by the photodiode array detector of the HPLC. As they did not absorb within

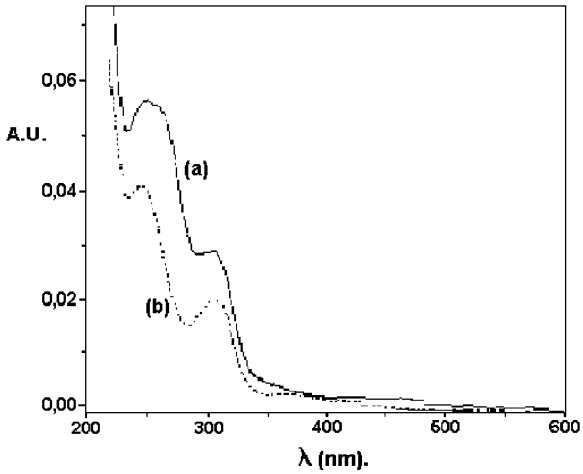
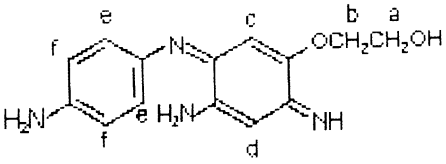


Fig. 4. UV–visible spectra of the two main transformation products of indamine: (a) B1; (b) B2.

Table 3
Main fragments of indamine photoproducts mass spectra (EI)

Analysed substances	Masses (amu)	Most abundant fragments (amu)
First photoproduct	284	65, 92, 128, 211, (238, low), 239
Second photoproduct	298	65, 92, 118, 133, 225, (238 and 239, low), 253

Table 4
Indamine and its photoproducts: chemical shifts of protons in MeOD[a]



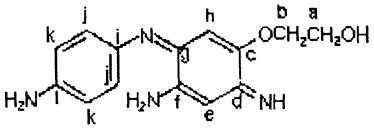
Analysed substances	δ (ppm)	Structure	Protons number	Protons
Indamine	4.10	Triplet	2	Ha
	4.25	Triplet	2	Hb
	6.20	Singlet	1	Hd
	6.62	Singlet	1	Hc
	6.97	Doublet	2	Hf
	7.27	Doublet	2	He
Photoproduct B1	4.10	Triplet	2	Ha
	4.25	Triplet	2	Hb
	7.05	Doublet + singlet	3	Hf, Hd
	7.30	Singlet	1	Hc
	7.40	Doublet	2	He
	8.15	Singlet	1	Hy
Photoproduct B2	2.55	Singlet	3	Hx
	4.07	Triplet	2	Ha
	4.15	Triplet	2	Hb
	6.75	Singlet	1	Hd
	7.03	Doublet	2	Hf
	7.20	Singlet	1	Hc
	7.25	Doublet	2	He

[a] x and y are the supplementary protons attributed to the photoproducts.

the visible spectrum range, they were probably not much conjugated. The products exhibited two absorption bands at 245 and 300 nm, a shoulder at 255 nm for B1 and two absorption bands at 245 and 305 nm for B2 (see Fig. 4).

Secondly, B1 and B2 photoproducts were also studied by electronic impact mass spectrometry. Two types of information were thus obtained. First, masses of the two blue hair dye photoproducts were obtained from their molecular ion $M^{\bullet+}$ by low resolution analysis: 284 amu for B1 and 298 amu for B2. These results were consistent with those obtained in the previous paper [22] on hair. Elimination of 45 amu (284–239 and 298–253 amu) and 28 amu (239–211 and 253–225 amu) was observed for indamine and the two

Table 5
Indamine and its photoproducts: chemical shifts of carbons in MeOD[a]



Analysed substances	δ (ppm)	Structure	Carbons
Indamine	61	C II	Ca
	72.3	C II	Cb
	92	C III	Ce
	100	C III	Ch
	116	C III	Ck
	128	C III	Cj
	140	C IV	Ci
	147	C IV	Cl
	152	C IV	Cc
	153.4	C IV	Cf
	160.1	C IV	Cg
	160.4	C IV	Cd
Photoproduct B1	62	C II	Ca
	72	C II	Cb
	95	C III	Ch
	105.7	C III	Ce
	117.1	C III	Ck
	126.8	C III	Cj
	127.6	C IV	Cd
	129.3	C IV	Cg
	135.8	C IV	Cf
	138.4	C IV	Ci
	148.1	C IV	Cl
	150	C IV	Cc
Photoproduct B2	13.8	C I	Cy
	62	C II	Ca
	72	C II	Cb
	95	C III	Ch
	104.4	C III	Ce
	117	C III	Ck
	126	C IV	Cx
	129	C III	Cj
	131	C IV	Cd
	135.6	C IV	Cg
	135.8	C IV	Ci
	147.5	C IV	Cl
	150.8	C IV	Cf
	151.5	C IV	Cc

[a] x is the supplementary carbon attributed to the photoproducts.

photoproducts corresponding, respectively, to $–CH_2CH_2OH$ and C=O fragments (Table 3). The fragment OCH_2CH_2OH (61 amu) is therefore present in the dye and the two photoproducts. Secondly, the molecular formulae of B1 and B2: $C_{15}H_{16}N_4O_2$ and $C_{16}H_{18}N_4O_2$, respectively, were provided by high resolution analysis. The difference of masses between photoproducts and the blue dye (12 and 26 amu) are explained by the addition of (=C–H) and (=C–CH_3) groups, respectively, and elimination of one proton.

Thirdly, the ^1H and ^{13}C NMR spectra were recorded in deuteriated methanol. The chemical shift values are reported in Tables 4 and 5, respectively. A supplementary proton Hy and Hx was detected, respectively, for B1 and B2 photoproducts, whereas Ha and Hb chemical shift remained the same for indamine and photoproducts, respectively. The molecule aromaticity was not altered although a low chemical shift showed a modification of the molecule. Quinonic protons were not observed and probably transformed into an aromatic ring (a deblinded singlet at 7.05 and 7.3 ppm for B1, and 6.75 and 7.2 ppm for B2 rose).

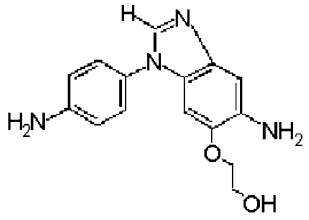
As a singlet appeared at 8.15 ppm for B1 and at 2.5 ppm for B2 and as 10, 11 and 13 protons were present, respectively, for the dye, B1 and B2, the extra carbons cannot be bounded to the other ones. Finally, ^{13}C NMR analysis confirmed ^1H NMR data, a supplementary carbon atom for B1 and two supplementary carbon atoms for B2 were detected.

4. Discussion and Conclusion

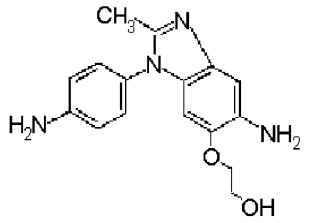
Thermal and photochemical transformations of dye on hair can be modelled in aqueous solutions containing both amino acids and dye. Our results are consistent with those of Cumming et al. [24] indicating that the dyes in the presence of histidine in a synthetic substrate are degraded in the same way as in a proteinic fibre and with those of Kramer [25] who reported that amino acid such as histidine should be responsible for the reduction process on wool. Barnes et al. [26] also noted that dye transformation is accelerated in the presence of amino acids such as cysteine.

Identification of the transformation products resulting from irradiation of an indamine aqueous solution in the presence of cysteine was realised by comparison of the retention times and UV–visible absorption spectra. Confirmation of the similarity with those obtained on hair was carried out by MS, NMR and IR spectroscopies. To summarise, different major information was collected:

1. The aromatisation of the quinone imine during the transformation was determined by IR spectroscopy.
2. The absence of alteration of the OCH_2CH_2OH group and aromatic nucleus was observed by mass and NMR spectroscopies.
3. An addition of groups on dye molecules was observed, as the photoproduct masses are higher than the dye mass. Mass spectrometry and NMR indicated that they are methyne (=C–H) and ethyne (=C–CH_3) units. These fragments cannot be bound to any aromatic ring as it would lead to a colouration, whereas our photoproducts are colourless. Thus, these fragments are added on the N-bridge.



Scheme 1. Indamine first transformation product, B1.



Scheme 2. Indamine second transformation product, B2.

In conclusion, the structures hypothesised are illustrated in Schemes 1 and 2; they are identical to the structures obtained for blue dye transformation on hair.

Finally, the mechanism exposed in our previous paper is also confirmed and detailed. Considering discolouration of indamine solution in the presence of L-cysteine, a two-step mechanism can be proposed:

- The first step would correspond to the reduction of the quinonic ring associated with the bleaching of the blue indamine solution in the presence of L-cysteine. By the way Kramer [25] reported that dye fading is usually an oxidative process on non-proteinic substrates, while reductive on protein fibres. Our hypothesis of dye reduction on hair is therefore consistent with this result.
- The second step is bimolecular. According to Duxbury [27,28], the substrate can be involved in the dye transformation. Hair can therefore participate to this second step and facilitates a bimolecular hair/dye reaction. However, as the same photoproducts are obtained in solution with concentrated dye (10^{-4} M), the dye would be concentrated enough in solution—or aggregated on hair—to enable a dye/dye mechanism.

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