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Bleaching of some photographic dyes by benzophenonekethyl radicals

SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Bleaching of some photographic dyes by benzophenone kethyl radicals.* Nota di Giancarlo Beggiato, Francesco Minto e Guido Pasini, presentata [*] dal Socio G. Semerano.

Riassunto. — È stato studiato il processo di riduzione di tre coloranti fotografici (uno di tipo pirazolonico (I), uno di tipo naftochinonimminico (II) ed un terzo di tipo benzoilacetanilidico (III) ad opera di radicali chetilici ottenuti irradiando, con luce di 366 nm, una soluzione di benzofenone, in presenza di substrati fornitori di idrogeno. Le esperienze sono state effettuate in due differenti ambienti: isopropanolo ed una soluzione benzenica di benzidrolo.

È stata pure studiata l'influenza di gruppi sostituenti nella molecola dell'agente riducente sul rendimento quantico del processo. È risultato, in particolare, che alcuni benzofenoni, sostituiti nelle posizioni 2 e 4 con gruppi NH_2 e OH, sono del tutto incapaci di ridurre la molecola del colorante sotto irradiamento.

La cinetica del processo di scomparsa del colore viene spiegata sulla base di un meccanismo a stadi, che giustifica l'ordine zero rispetto alla concentrazione del colorante ed il primo ordine rispetto alla intensità della luce assorbita.

Introduction

The dyes used in colour photography are generally quite stable under direct irradiation with UV and visible light. The bleaching of the dyes becomes, however, a fast process when benzophenone kethyl radicals are the reductive agents. The radicals are easily produced by irradiation of benzophenones in the presence of substrates from which hydrogen can be extracted.

W. F. Smith jr. and B. W. Rossiter [1] have studied the reduction process of a pyrazolone azomethine dye in the presence of benzophenone and benzhydrol in benzene.

We have extended this research to the three main dyes of photographic interest (magenta I, cyan II, and yellow III).

Experiments were also carried out with various benzophenones in two different media: isopropanol and a benzenic solution of benzhydrol.

Experimental

The dyes were synthetized in the Ferrania Laboratories of 3 M Italia S.p.A.. Benzophenone, benzhydrol, benzene and isopropanol were Carlo Erba RP, RS, RS–ACS grade products. Traces of thiophene were removed from benzene by standard methods. Substituted benzophenones (see Table I) (Aldrich, Fluka, Eastman Organic Chemicals, K & K products) were purified by recrystallization from water-ethanol mixture or *n*-hexane. The absorption

(*) Nella seduta del 10 maggio 1975.

spectra were recorded with a Perkin-Elmer 356 double-beam spectrophotometer and the kinetics of colour fading were followed with a Perkin–Elmer 139 single-beam spectrophotometer, at 508 nm (absorption maximum) for dye I, 670 nm (absorption maximum) for dye II and 470 nm for dye III. Only for dye III the kinetics were not followed at the absorption maximum (427 nm)
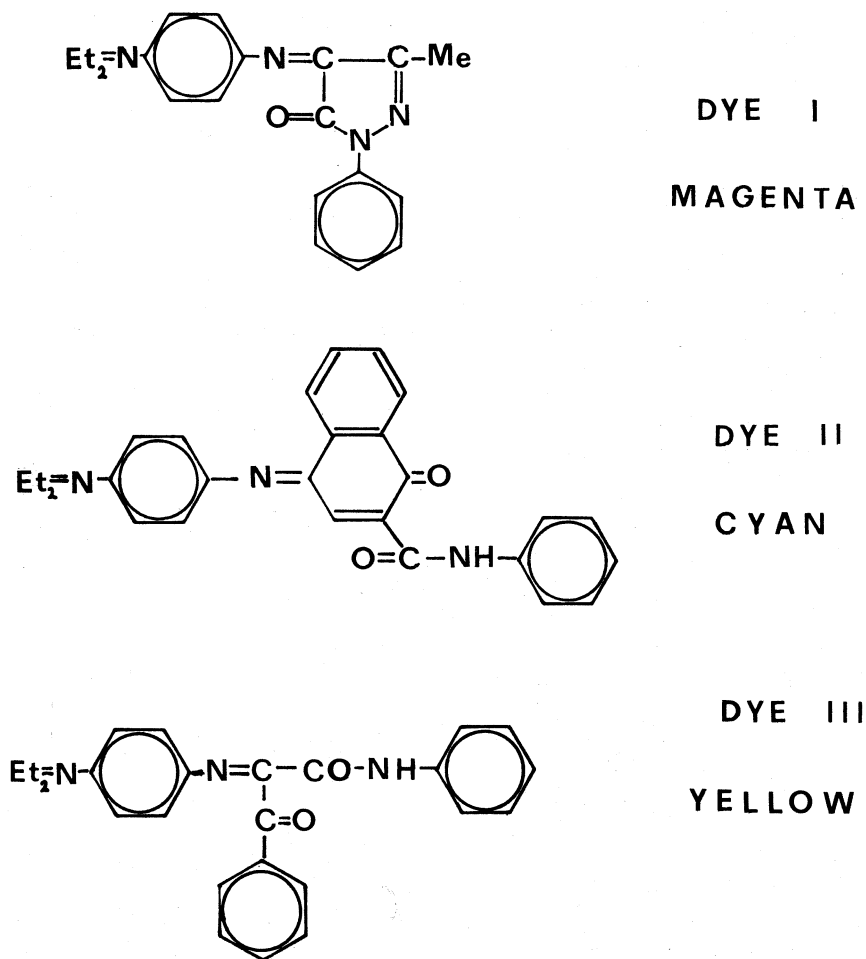

Fig. 1. – Structural formulas of the three dyes: I (Magenta), II (Cyan) and III (Yellow).

in order to avoid any spectral interpherence by the benzophenones. The samples, degassed and sealed in a quartz-windowed cell, were irradiated with an XBO 900 W Hanovia xenon arc lamp at 366 nm wavelength, selected by a Hilger-Watts monochromator, under conditions where the incident light was totally absorbed by the benzophenone. At the irradiation wavelength, the dyes absorbed a very small fraction of light with respect to the benzophenones at the concentrations used (for benzophenones: $3 \cdot 10^{-2}$ M; for benzhydrol: 0.5 M; for the dyes: less that $4 \cdot 10^{-5}$ M).
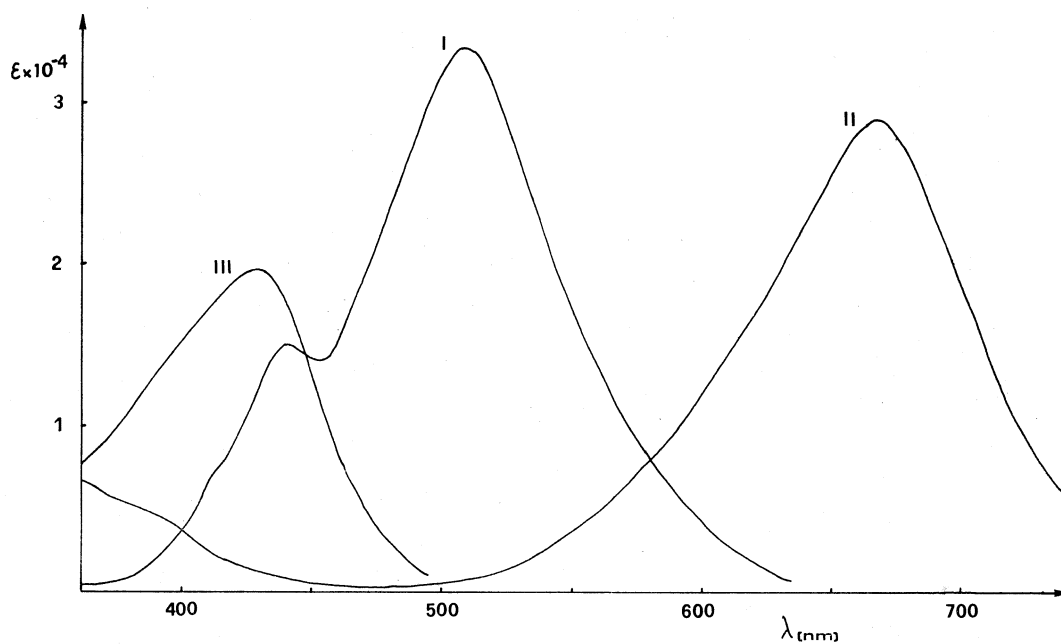
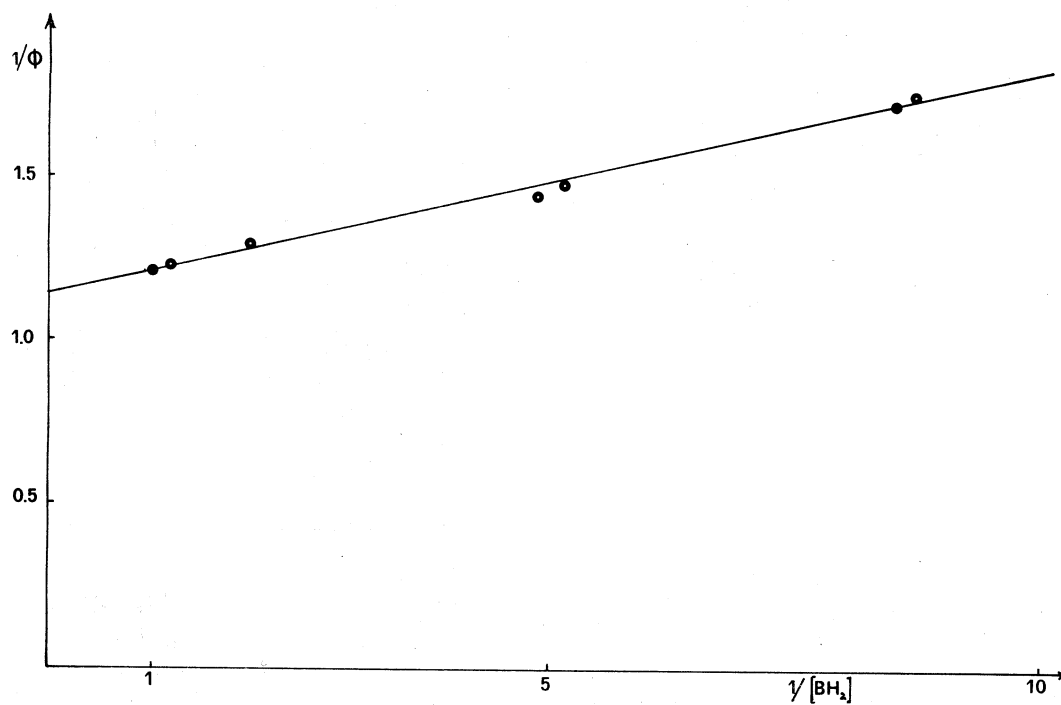Fig. 2. – Spectra of the three dyes: I (Magenta), II (Cyan) and III (Yellow).

Fig. 3. – Plot $1/\emptyset$ *vs* $1/[BH_2]$ for the bleaching of the dye I (see Table III).

The absorbance was negligible for dye I; in the case of dyes II and III, the absorbance was corrected by substracting the light absorbed by the dyes from the total incident light.

The light intensity was measured by Parker-Hatchard actinometry [2].

RESULTS AND DISCUSSION

On Table I are collected the bleaching quantum yields for the three dyes at constant light intensity and benzhydrol concentration. The ∅ values indicate that not all the benzophenones are able to produce bleaching of the dyes. When bleaching occurs, it appears from absorbance/time plots that the fading rate is constant up to the end of the process.

TABLE I.

Bleaching quantum yields ($\varnothing$) of dyes I, II *and* III *in the presence of different benzophenones.*

Benzhydrol concentration : 0.5 M
Light intensity : 8.3×10^{-8} einstein $l^{-1} s^{-1}$

Benzophenone \ Dye	Magenta (I)	Cyan (II)	Yellow (III)
H	0.77	0.84	0.97
4-CH$_3$	0.83	0.75	0.83
4,4'-di-CH$_3$	0.89	0.83	0.95
4,4'-di-CH$_3$O	0.80	0.88	0.87
4,4'-di-Cl	0.86	0.85	0.85
4-Br	0.77	0.73	0.84
2-Cl-4-F	0.70	0.75	0.83
4-NH$_2$	0.00	0.00	0.00
4-N (CH$_3$)$_2$	0.00	0.00	0.00
2-NH$_2$	0.00	0.00	0.00
2-OH	0.00	0.00	0.00

With the three dyes studied, the bleaching process is zero order in dye concentration and first order in light intensity.

This result has been already observed [1] for the photoreduction of a pyrazolone azomethine compound (very similar to dye I) by unsubstituted benzophenone.

TABLE II.

Bleaching quantum yields of dye I by benzo-phenones at different light intensities [*] *and constant benzhydrol concentration* (0.5 M).

I_o	$\varnothing$
1.5×10^{-7}	0.76
8.3×10^{-8}	0.77
4.0×10^{-8}	0.78
1.5×10^{-8}	0.75

(*) Einstein $l^{-1} s^{-1}$.

Table II shows that, at constant benzhydrol concentration, the quantum yield is independent of the absorbed light intensity in the range $1.5 \cdot 10^{-8} \div 1.5 \cdot 10^{-7}$ einstein $l^{-1} s^{-1}$. At constant light intensity, the bleaching quantum yield depends on the benzhydrol concentration (see Table III).

TABLE III.

Bleaching quantum yields of dye I by benzo-phenone at different benzhydrol concentrations and constant light intensity $(I_0 = 8.3 \times 10^{-8}$ *einstein* $l^{-1} s^{-1}$; *dye concentration* $= 2 \times 10^{-5}$ M$)$.

Benzhydrol concentration (M)	$\varnothing$
0.960	0.82
0.830	0.81
0.500	0.77
0.200	0.70
0.190	0.67
0.116	0.58
0.114	0.57

For all the dyes a straight line was obtained when $1/\varnothing$ was plotted against $1/[BH_2]$, where $[BH_2]$ is the benzhydrol concentration.

The simplest kinetic mechanism which agrees with the experimental data is this one already proposed by Smith and Rossiter [1]:

$$1) \quad B \xrightarrow{\ I_0\ } {}^3B$$

$$2) \quad {}^3B \xrightarrow{\ k_2\ } B$$

(I)

$$3) \quad {}^3B + BH_2 \xrightarrow{\ k_3\ } 2\,BH^{\bullet}$$

$$4) \quad BH^{\bullet} + D \xrightarrow{\ k_4\ } B + DH^{\bullet}$$

$$5) \quad BH^{\bullet} + DH^{\bullet} \xrightarrow{\ k_5\ } B + DH_2$$

$$6) \quad 2\,DH^{\bullet} \xrightarrow{\ k_6\ } D + DH_2$$

where: B = benzophenone;

BH$_2$ = benzhydrol;

D = dye.

Applying the steady state hypothesis to the intermediates ${}^3B$, $BH^{\bullet}$ and $DH^{\bullet}$, we obtain an expression for the fading rate:

$$(2) \qquad\qquad v = \frac{I_0 \cdot k_3 \cdot [BH_2]}{k_2 + k_3 \cdot [BH_2]}$$

so that

$$(3) \qquad \varnothing = \frac{k_3 \cdot [BH_2]}{k_2 + k_3 \cdot [BH_2]} \qquad \text{or} \quad 1/\varnothing = 1 + \frac{k_2}{k_3 \cdot [BH_2]} \ .$$
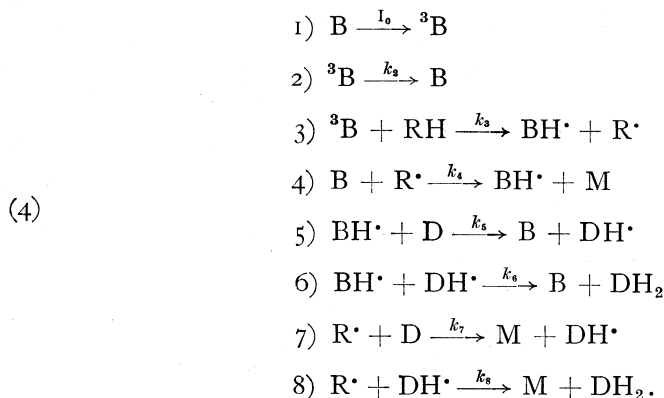
This is identical to that found for the photoreduction of benzophenone to benzopynacol. Bell and Linschitz [3] obtained values of $k_2 = 1.2 \cdot 10^5 \, s^{-1}$, $k_3 = 2.3 \cdot 10^6 \, M^{-1} \, l^{-1} \, s^{-1}$ by kinetic measurements. Therefore, the quantum yield increases asymptotically to 1 by raising the benzhydrol concentration. At the concentrations used, the values obtained were slightly different from those expected from the relationship (3), using the rate parameters of literature. In the particular case of dye I, a very good agreement with the value obtained by Smith and Rossiter was found.

The fact that the quantum yield obtained for dyes I and II were less than predicted from literature values, could be explained by taking into account the contribution of a reaction which restores the dye: $BH^{\bullet} + DH^{\bullet} \to BH_2 + D$, while the higher values obtained for dye III could be justified by a dimerization step: $2\,DH^{\bullet} \to DH\text{—}DH$.

This explains the values for the intercept and the slope in the plot $1/\varnothing$ vs $1/[BH_2]$ (see fig. 3). From these parameters a value of 0.06 for the ratio k_2/k_3 was obtained, which is in good agreement with values found previously [3, 4].

In isopropanol (RH) ∅ values higher than in benzene + benzhydrol were found for benzophenone. The values for the three dyes were similar and close to one.

Assuming that the dye can either be reduced by kethyl or by solvent radicals, a mechanism can be postulated which agrees with the experimental results:

(4)

$$1) \quad B \xrightarrow{\ I_0\ } {}^3B$$

$$2) \quad {}^3B \xrightarrow{\ k_2\ } B$$

$$3) \quad {}^3B + RH \xrightarrow{\ k_3\ } BH^{\cdot} + R^{\cdot}$$

$$4) \quad B + R^{\cdot} \xrightarrow{\ k_4\ } BH^{\cdot} + M$$

$$5) \quad BH^{\cdot} + D \xrightarrow{\ k_5\ } B + DH^{\cdot}$$

$$6) \quad BH^{\cdot} + DH^{\cdot} \xrightarrow{\ k_6\ } B + DH_2$$

$$7) \quad R^{\cdot} + D \xrightarrow{\ k_7\ } M + DH^{\cdot}$$

$$8) \quad R^{\cdot} + DH^{\cdot} \xrightarrow{\ k_8\ } M + DH_2.$$

The first four steps of this mechanism are the same as postulated in the kinetic scheme of the photoprocess between benzophenone and isopropanol, the product M being acetone [5].

We obtain an expression:

$$v = \frac{I_0 \cdot k_3 \cdot [RH]}{k_2 + k_3 \cdot [RH]}$$

for the rate of the fading process, which could explain the close-to-one quantum yields found in isopropanol, if k_2 is negligible with respect to $k_3 \cdot [RH]$.

Comparing the quantum yields of Table I, obtained with substituted benzophenones, no clear trend was found in the substituent effect on the rate of the fading process.

It may be seen, however, from Table I, that some benzophenones, substituted in positions 2 and 4 with NH_2 and OH groups, are completely unable to bleach the dyes under irradiation, either in benzene + benzhydrol or in isopropanol.

This may be explained on the basis of an intramolecular CT nature of the lowest triplet state of the benzophenone molecule, with a lower energy than the $n\pi^*$ reactive state [6, 7], or, for the *ortho*-derivatives, on the basis of an intramolecular keto-enolic equilibrium between the carbonyl and the hydrogen atom of NH_2 or OH group.

From the literature we know that the *para*-hydroxy- and *para*-amino-benzophenones exhibit very low triplet yield values, relative to that of benzophenone, as determined in benzene solution from intensity measurements of the sensitized biacetyl phosphorescence; the *ortho*-amino- and *ortho*-hydroxy-derivatives do not sensitize at all [8].

The peculiar behaviour of these benzophenones agrees with the well known application of 2-OH-benzophenones in colour photography as stabilizers against UV radiations [9].

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