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Photodegradation of Some 1:2 Metal Complexed Azo Dyes in an Amide Environment

Jolanta Sokołowska-Gajda

Institute of Dyes, Technical University (Lodz), 90-924 Lodz, Zwirki 36, Poland

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ABSTRACT

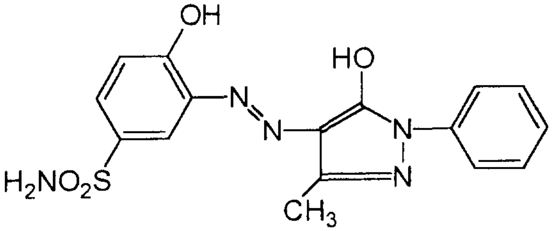
The photodegradation of some metallized azo dyes was investigated. The photofading was done in DMF using 300 nm, 350 nm and daylight irradiation. The quantum yield Φ of the photodegradation performed under UV light was measured and it was found that the metal present in the molecule of dye and the photolysis wavelength influence this process significantly. The presence of a ketone sensitizer like benzophenone accelerates the photofading of dyes, confirming that hydrogen abstraction is responsible for their degradation. It was observed that oxygen plays a very important role in the photolytic behaviour of the studied dyes under daylight exposure. Co(III) complexed azo dyes, contrary to Cr(III) and Fe(III) analogues, were found to be effective singlet oxygen quenchers. Additionally, the expected relationship between log Φ and the reciprocal of lightfastness was found. © 1997 Elsevier Science Ltd

Keywords: metallized azo dyes, photodegradation, amide environment, lightfastness.

INTRODUCTION

It has been known for some time that the treatment of suitable dyes with Cr, Co and Cu salts usually improves their lightfastness. Since the manufacture of metallized dyes and their application to wool, nylon and leather results in the presence of heavy metals ions currently considered as the priority pollutants of effluents, there is the great interest in the synthesis of more environmentally safe 1:2 Fe complexed dyes [1, 2]. A key objective of this study is to compare the lightstability of some 1:2 chromium, cobalt and iron complexed azo dyes, as presented by Schemes 1 and 2.

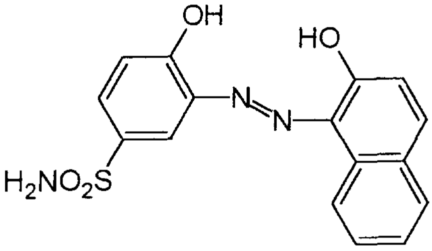
Although metallized dyes are a commercially very important class of colorants, there are relatively few studies concerning their photolytic behaviour.



I

Dye	Type of complex
Ia	1 : 2 Fe
Ib	1 : 2 Co
Ic	1 : 2 Cr

Scheme 1



II

Dye	Type of complex
IIa	1 : 2 Fe
IIb	1 : 2 Co
IIc	1 : 2 Cr

Scheme 2

Chang and Miller [3] investigated the photostability of some metal complexed azo dyes in N-ethylacetamide (nylon model) under aerobic and anaerobic conditions. Graves [4] *et al.* studied the effect of metallization of azo dyes (mostly 1:1 Me complexes) under aerobic conditions and they found that the dyes with metal ions having low lying excited states suppress singlet oxygen formation completely. Recently the photodegradation of some 1:2 Me complexed formazan dyes [5] was investigated and the quantum yield Φ of this process was also measured. In the present work the photodegradation of the 1:2 Me complexed azo dyes **I** and **II** in DMF solution under aerobic and anaerobic conditions using 300 nm and 350 nm irradiation is determined. Additionally their photodegradation under daylight in the presence of Methylene Blue and DABCO is also reported.

RESULTS AND DISCUSSION

The photodegradation of some chromium, cobalt and iron complexed azo dyes **I** and **II** was conducted in DMF solution at 300 nm and 350 nm irradiation under aerobic and anaerobic conditions. These results are presented in Table 1. It is evident that the photostability of the examined dyes strongly depends on the metal present in their molecules. The best photostability is shown by the 1:2 Co complexed azo dyes, whereas the 1:2 Cr and 1:2 Fe complexes are less stable. The presence of air during photodegradation does not affect this process significantly. Slight increase of the photostability is only observed in the case of 1:2 Fe complexed dyes **Ia** and **IIa**, which may suggest a tendency for the reoxidation of their partially reduced complexes. In other cases the photostability of dyes derived from chromium and cobalt salts is similar, or the same, under both conditions, i.e., in the presence of nitrogen and air. It is likely that the photodegradation of dyes **I** and **II** proceeds via reduction involving hydrogen abstraction from DMF, which is considered to be a hydrogen-donating solvent [6]. The photodegradation quantum yield Φ of dyes **I** and **II** is low, but in the presence of a ketonic sensitizer like benzophenone, it is significantly increased, thus evidencing that hydrogen abstraction is involved in their photodegradation. It is also observed for dyes **Ia–Ic** that the influence of benzophenone present during 300 nm irradiation under air is similar to that observed for the same experiment performed under nitrogen. Presented data (Table 1) clearly indicate that the photodegradation of dyes **I** and **II** depends on the irradiation source, and that the quantum yield Φ of this process increases as the photolysis wavelength decreases. This observation is common for dyes. Irick [7, 8] *et al.* and Albini [9] documented an increase of the photodegradation quantum yield Φ of azo dyes with decreasing wavelength in different media including polyamide film.

For further evaluation of the role of oxygen in the photofading of dyes **I** and **II**, their daylight photodegradation in DMF solution in the presence of DABCO and a singlet oxygen sensitizing dye such as Methylene Blue was also conducted. The results of these experiments are shown in Table 2.

It is evident that the 1:2 Fe and 1:2 Cr complexed azo dyes exhibit self-sensitized conversion in the presence of air, which is clearly inhibited in the presence of DABCO. Addition of Methylene Blue to DMF solutions of these dyes accelerates the photodegradation of the chromium and iron derivatives, whereas the cobalt complexes show a very high stability. These observations are consistent with conclusions formulated earlier for 1:1 metallized azo dyes [4] and 1:2 metallized formazan dyes [5]. Dyes reactivity towards singlet oxygen depends on the value of the energy of the lowest excited state of the metal ion used for the metallization, in comparison with the triplet state energy of the dye [4]. Triplet state energies [4] of dyes **I** and **II** were estimated to lie between 0.45–0.65 of the singlet energy level (obtained from λ_{max} of the dye), and were compared with the energy of the lowest excited states of Co(III), Cr(III) and Fe(III) ions (Table 3).

TABLE 1
Photodegradation Quantum Yields[a] and Lightfastness of Dyes **I** and **II**

Dye	*L F*	*Photodegradation quantum yields* (Φ)		*Photostability* (Φ^{-1})		*log* Φ	
		N_2	*Air*	N_2	*Air*	N_2	*Air*
Ia	6–7	$3.57 \cdot 10^{-4}$	$2.84 \cdot 10^{-4}$	2800	3500	−3.4473	−3.5466
		$1.67 \cdot 10^{-4}$[b]	$1.18 \cdot 10^{-4}$[b]	5990[b]	8470[b]	−3.7772	−3.9281
		$1.05 \cdot 10^{-2}$[c]	$1.05 \cdot 10^{-2}$[c]	95[c]	95[c]		
Ib	8	$2.60 \cdot 10^{-5}$	$2.80 \cdot 10^{-5}$	38460	35714	−4.5850	−4.5528
		$5.22 \cdot 10^{-6}$[b]	$5.22 \cdot 10^{-6}$[b]	191570[b]	191570[b]	−5.2823	−5.2823
		$1.40 \cdot 10^{-3}$[c]	$1.50 \cdot 10^{-3}$[c]	714[c]	714[c]		
Ic	6–7	$2.06 \cdot 10^{-4}$	$2.06 \cdot 10^{-4}$	4850	4850	−3.6861	−3.6861
		$1.30 \cdot 10^{-4}$[b]	$1.30 \cdot 10^{-4}$[b]	7690[b]	7690[b]	−3.8860	−3.8860
		$9.90 \cdot 10^{-3}$[c]	$1.09 \cdot 10^{-2}$[c]	101[c]	92[c]		
IIa	6–7	$2.94 \cdot 10^{-4}$	$2.26 \cdot 10^{-4}$	3400	4420	−3.5314	−3.6458
		$3.12 \cdot 10^{-5}$[b]	$2.87 \cdot 10^{-5}$[b]	32000[b]	34840[b]	−4.5051	−4.5421
		$2.16 \cdot 10^{-3}$[c]		462[c]			
IIb	8	$5.65 \cdot 10^{-5}$	$6.00 \cdot 10^{-5}$	17700	16666	−4.2479	−4.2218
		$8.02 \cdot 10^{-6}$[b]	$8.02 \cdot 10^{-6}$[b]	124688[b]	124688[b]	−5.0958	−5.0958
		$2.23 \cdot 10^{-3}$[c]		448[c]			
IIc	7+	$8.74 \cdot 10^{-5}$	$9.90 \cdot 10^{-5}$	11440	10000	−4.0584	−4.0043
		$1.57 \cdot 10^{-5}$[b]	$1.57 \cdot 10^{-5}$[b]	63816[b]	63816[b]	−4.8049	−4.8049
		$2.30 \cdot 10^{-2}$[c]		43[c]			

[a] The photolysis was run under 300 nm inradiation. [b] The photolysis was run under 350 nm irradiation. [c] The photolysis was run in the presence of benzophenone (0.027m/1) under 300 nm irradiation.

It is apparent that chromium and iron complexed azo dyes **I** and **II** having lower or similar triplet level energy in comparison with the energy level of Fe(III) and Cr(III) ions do not quench singlet oxygen, thus causing their faster degradation. Only cobalt complexes are very stable; they contain a cobalt ion with a low lying excited state, which suppresses singlet oxygen formation and thus protects them from the fading process.

All photostability investigations of dyes **I** and **II** conducted under aerobic and anerobic conditions at 300 nm and 350 nm irradiation and under daylight irradiation in DMF in the presence of air showed a good quantitative relationship, consistent with their photostability on polyamide fabric.

As the next step of this study, a correlation between the log of the photodegradation quantum yield Φ ($\log\Phi$) at 300 nm and 350 nm under anaerobic and aerobic conditions in DMF and the reciprocal of the lightfastness on polyamide fabric was made. Least square analysis of the data gives good relationship for all these cases (eqns 1–4) (Figs 1–4).

TABLE 2

*The Extent of Daylight Photolysis of Dyes I and II

Dye	*Self-sensitized conversion (%)*	*Self-sensitized conversion with DABCO[a] (%)*	*Conversion with Methylene Blue[b] (%)*
Ia	7.4	2.7	53.7
Ib	1.0	1.0	1.0
Ic	15.2	8.7	32.6
IIa	8.9	2.5	60.7
IIb	0.5	0.5	0.5
IIc	18.2	6.0	42.8

*After eight days.

[a] DABCO was used at concentration 0.0327 m/l.

[b] Methylene Blue was used at $4.75 \cdot 10^{-5}$ m/l.

TABLE 3

Energy Levels of Dyes I and II Excited States

Dye	λ_{max} *(nm)*	ε	$E_{singlet}$ *(cm⁻1)*	$E_{triplet}$ (cm^{-1})
Ia	446	25 400	22 420	10 089–14 570
Ib	454	34 000	22 000	9900–14 300
Ic	470	36 800	21 270	9575–13 830
IIa	480	20 700	20 830	9374–13 540
IIb	564	27 200	17 730	7979–11 525
IIc	568	20 800	17 600	7920–11 440

Energy of the lowest excited state of Fe(III)[10] is 13 000 cm^{-1} ($6 \cdot H_2O$). Energy of the lowest excited state of Co(III)[11] is 7800 cm^{-1} ($6 \cdot H_2O$). Energy of the lowest excited state of Cr(III)[12] is 15 000 cm^{-1} ($6 \cdot H_2O$).

$$\log \Phi_{300}(N_2) = -8.18 + 30.06/LF \qquad r = 0.95 \qquad (1)$$

$$\log \Phi_{300}(O_2) = -7.66 + 26.27/LF \qquad r = 0.95 \qquad (2)$$

$$\log \Phi_{350}(N_2) = -10.19 + 39.78/LF \qquad r = 0.90 \qquad (3)$$

$$\log \Phi 350(O_2) = -9.89 + 37.30/LF \qquad r = 0.91 \qquad (4)$$

These and previously [5] obtained results for 1:2 Me complexed formazan dyes **III** clearly indicate that DMF is suitable model solvent for the quantitative, and sometimes qualitative [3], characterisation of the photolytic behaviour of 1:2 Me complexed dyes.

As a final conclusion of this and previous studies [5], it was also found for 300 nm irradiation (under nitrogen and air) that a good correlation between logΦ and the reciprocal of the lightfastness of 1:2 azo and 1:2 formazan dyes (Scheme 3) exists (eqns 5 and 6) (Figs 5 and 6).

$$\log \Phi_{300}(N_2) = -7.02 + 21.27/LF \qquad r = 0.91 \qquad (5)$$

$$\log \Phi_{300}(O_2) = -7.94 + 27.82/LF \qquad r = 0.92 \qquad (6)$$

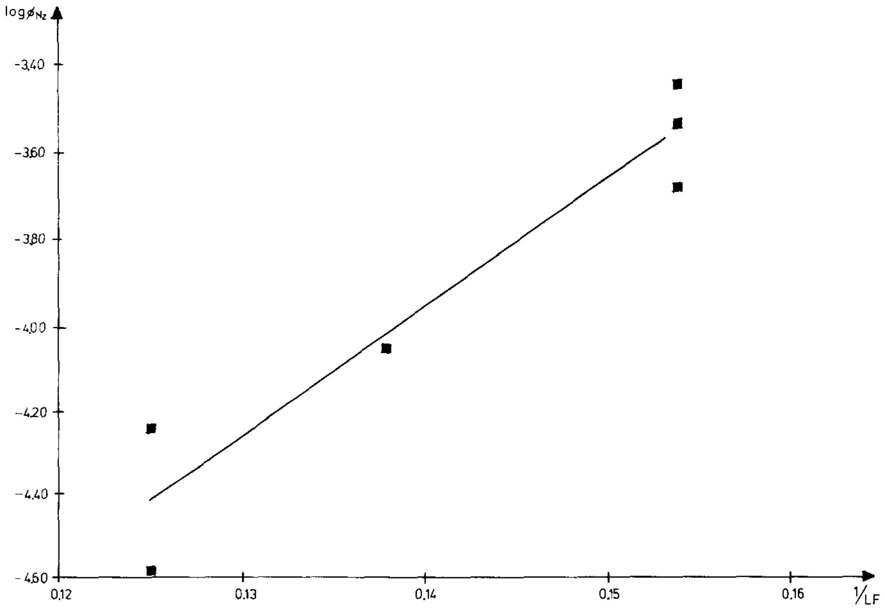


Fig. 1. Relationship between log$\Phi_{300}(N_2)$ and the reciprocal of lightfastness (LF).

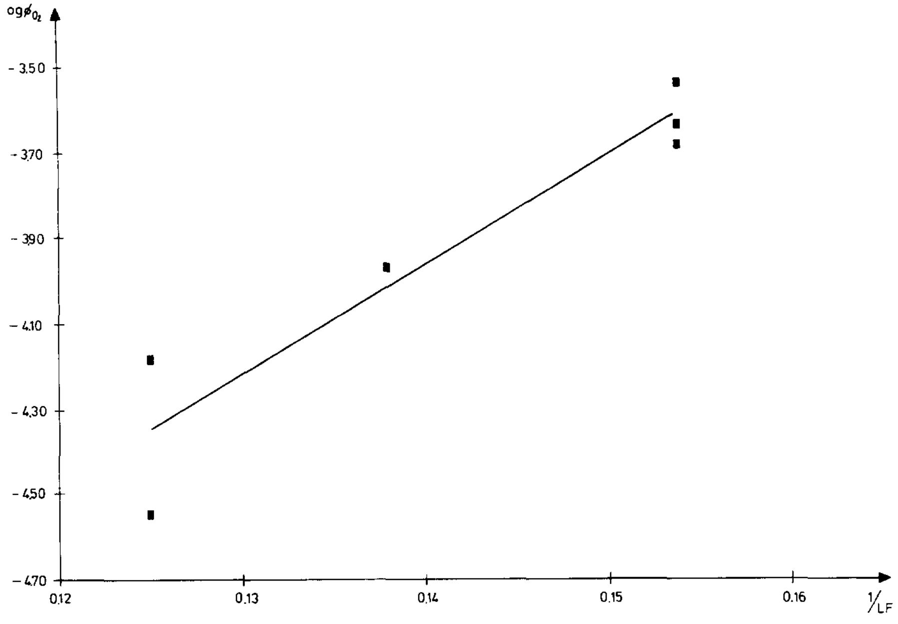


Fig. 2. Relationship between $\log\Phi_{300}(O_2)$ and the reciprocal of lightfastness (LF).

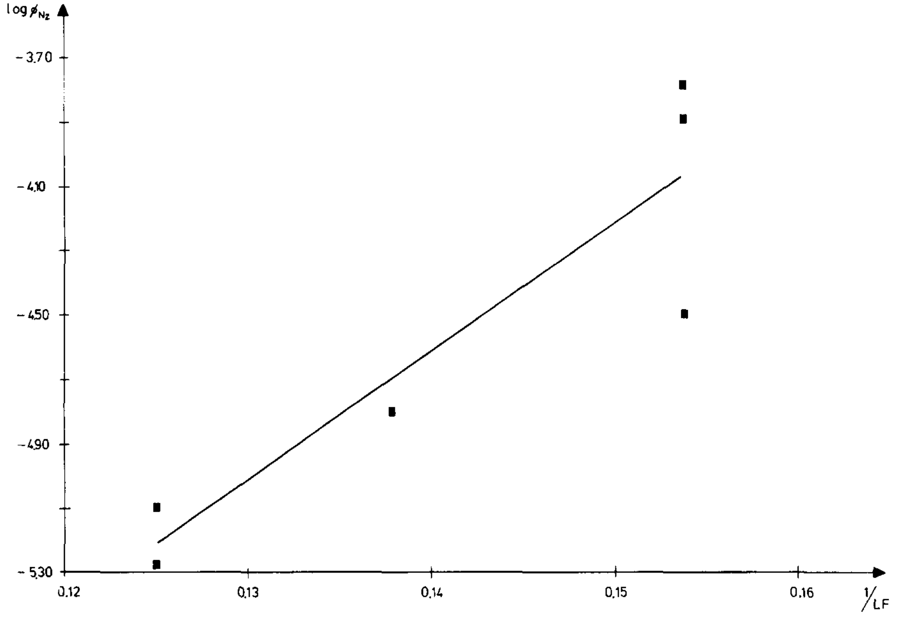


Fig. 3. Relationship between $\log\Phi_{350}(N_2)$ and the reciprocal of lightfastness (LF).

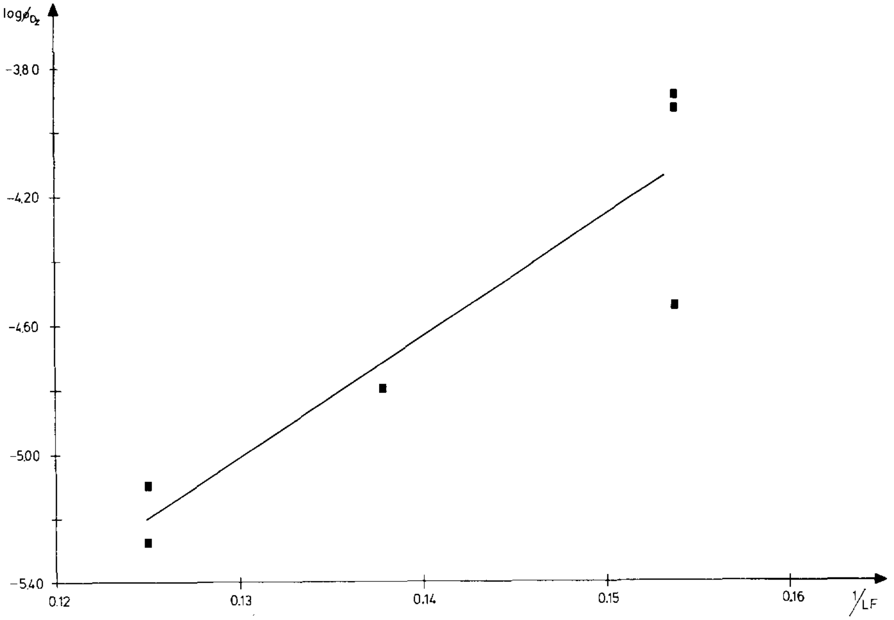


Fig. 4. Relationship between log$\Phi_{350}(O_2)$ and the reciprocal of lightfastness (LF).

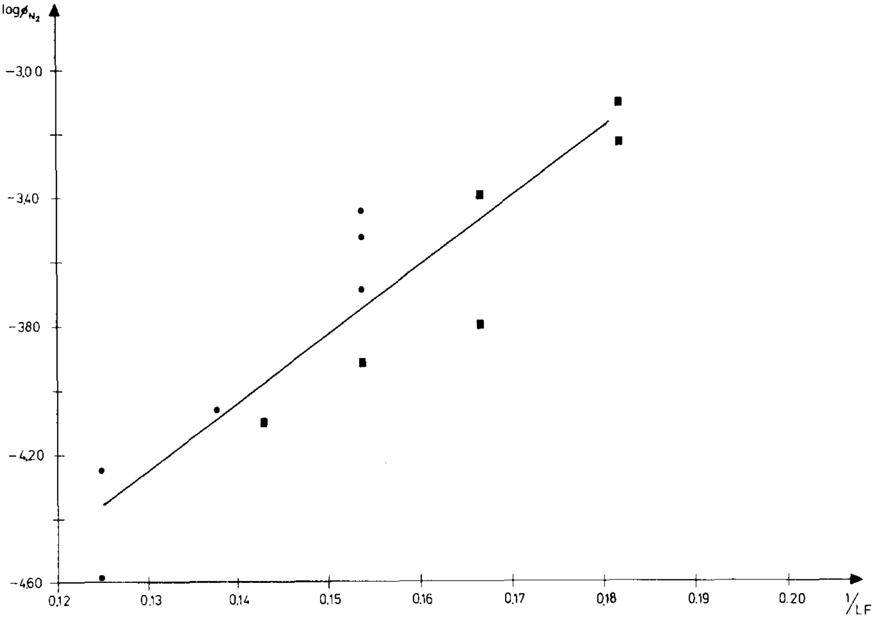


Fig. 5. Relationship between log$\Phi_{300}(N_2)$ and the reciprocal of lightfastness (LF) for azo (●) and formazan (■) dyes.

EXPERIMENTAL

The metallized dyes **I** used in this investigation were synthesized according to the methods described in the literature [1] and purified by crystallization. The purity of the dyes was checked by TLC. Dye solutions ($5 \cdot 10^{-5}$ mol/l) in freshly distilled DMF placed in a quartz vessel were faded in a Rayonet photolytic reactor RPR-200 (The Southern New England Ultraviolet Company, USA) equipped with eight 300 nm or 350 nm lamps, which according to their specification, have a satisfactorily narrow region of emission. Anaerobic and aerobic conditions were achieved by bubbling dry nitrogen or air into the solution for 30 min before irradiation. Fading was followed by the decrease in absorption at λ_{max} of the dye. Since the dye solutions obeyed the Lambert-Beer law, the concentration of the remaining dye was determined spectrophotometrically (when necessary, appropriate dilution of the dye solution was made). The visible spectra were recorded on a Specord M-40 UV-VIS spectrophotometer (C. Zeiss, Jena).

The intensity of the photolysis lamps was determined using uranyl oxalate actinometry [4]. The actinometer was prepared by treating the solution of uranyl sulfate with excess of oxalic acid placed in the same quartz vessel in an exactly equivalent position to the examined dye solution and irradiated.

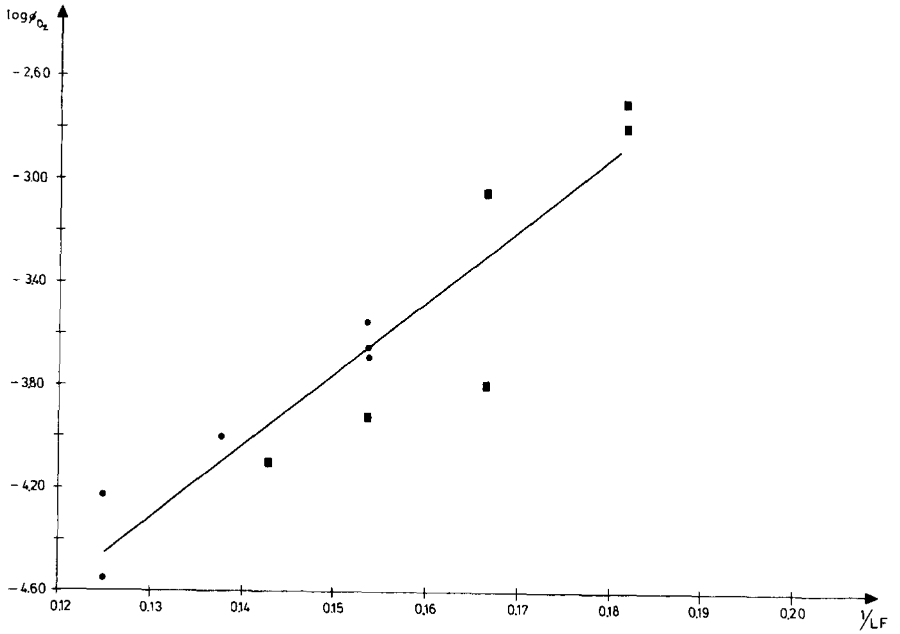
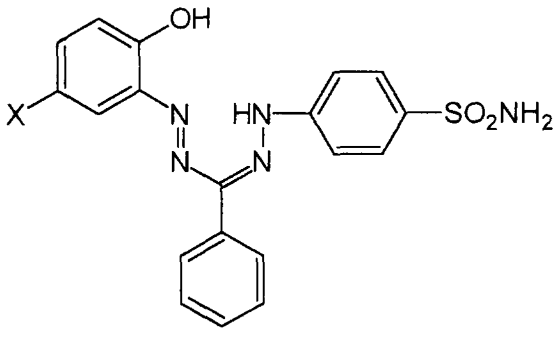


Fig. 6. Relationship between $\log\Phi_{300}(O_2)$ and the reciprocal of lightfastness (LF) for azo (●) and formazan (■) dyes.



III

Dye	X	Type of complex	log$\Phi(N_2)$	log$\Phi(O_2)$
IIIa	NO_2	1 : 2 Fe	-3.3979	-3.0550
IIIb	Cl	1 : 2 Fe	-3.2291	-2.7958
IIIc	H	1 : 2 Fe	-3.1079	-2.6989
IIId	NO_2	1 : 2 Co	-4.0969	-4.0969
IIIe	Cl	1 : 2 Co	-3.9208	-3.9208
IIIf	H	1 : 2 Co	-3.7958	-3.7958

Scheme 3

The decrease in oxalate concentration during photolysis was measured on the basis of the difference in the amount of potassium permanganate[15] (in the presence of sulfuric acid) used in the titration of the same volume of unilluminated and illuminated actinometer solution. The intensity of absorbed light, i.e. the number of quanta per second absorbed by the system, was calculated based on the amount of oxalate molecules decomposed in time of photolysis from known quantum yields disappearance of oxalate molecules per quantum ($\Phi_{300} = 0.57$ [14], $\Phi_{350} = 0.49$ [14]). Since the dye solutions showed complete absorption under photolysis conditions (4Π geometry of merry-go-around unit with centrally placed photolysed sample surrounded with symmetrically located lamps, the proper concentration and thickness of the dye solution layer, small photolysis extent $= 15\%$) the quantum yield of fading of the dyes was calculated from the number of dye molecules decomposed and the number of quanta absorbed in the same time. The values of quantum yields Φ were estimated as an average from at least three determinations, and their accuracy was $\pm 10\%$. 2% polyamide dyeings of dyes were used for lightfastness (LF) determination. The lightfastness was measured on a Xenotest apparatus (Hanau) according to Polish Standards, which correspond to British Standards [16].

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