

**16. *Chemical and Photochemical Degradation of Anthraquinone Mordant Dyes in Methanol. Part II.***<sup>1</sup>

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The degradation of 3-nitro-alizarin and -purpurin in methanol in presence of air under irradiation by a mercury-vapour lamp or sunlight is described.

FADING of dyes in light is usually a reaction with a low quantum yield and accordingly very slow, with only very small yields, which render the isolation and identification of products rather difficult. The photochemical degradation of 3-nitro-alizarin and -purpurin in methanol has now been compared with their oxidation by lead dioxide and potassium permanganate.<sup>1</sup> The solvent used in the photochemical degradation contained 2% of acetic acid because the acidity of the solution had a marked influence on the course of the reactions. Fading of the dye solutions was carried out with the use of mercury-vapour lamps (Philips HP 125 w and SP 500 w) and in sunlight. The vessels containing the irradiated solutions were made of Pyrex glass, so that only the radiation of wavelengths longer than 300 m $\mu$  was active, *i.e.*, for the mercury-vapour lamps 313, 365, 405, 546, and 578 m $\mu$ .

<sup>1</sup> Part I, preceding paper.

## EXPERIMENTAL AND RESULTS

*Analysis of Partly Faded Solutions of 3-Nitro-alizarin and -purpurin.*—In an investigation of the products of photochemical degradation where maximum concentrations of the first products must be obtained, the irradiation time is more important than the initial dye concentration. Fading of concentrated solutions does not result in high concentrations of the first fading products but only renders separations more difficult. Therefore dilute solutions were used, namely, 0.32—1.75 mmole/l. (SP 500 w), 0.10—0.21 mmole/30 ml. (HP 125 w), and 0.07—0.19 mmole/50 ml. (sunlight).

Experiments with the HP 125 w mercury-vapour lamp were carried out by placing Pyrex-glass cuvettes (contents 30 ml.) 12 cm. from the lamp; the cuvettes were cooled by air from a fan placed under the lamp. Fading with light from the SP 500 w water-cooled mercury-vapour lamp (undirected radiation) was carried out in a 1-l. Pyrex-glass vessel with a cooling spiral and a tube in the centre of the vessel holding the lamp; the solutions were cooled by circulating water from a thermostat bath. For fading with sunlight, cuvettes (contents 50 ml.) were exposed to direct sunlight during July and August. In all the experiments the solutions were in direct contact with the air. Stirring the solutions or saturating them with oxygen did not accelerate fading appreciably.

Partly faded solutions were analysed by chromatography on paper strips (Whatman no. 1) (see Table 1). Solutions of small amounts of the products were obtained by cutting out the bands on the chromatograms and extracting them with methanol. The absorption spectra of the products in ultraviolet and visible light have been measured (Unicam SP 500 quartz spectrophotometer). The chromatographic properties and the absorption spectra of the products were then compared (simultaneous chromatograms on one paper) with those corresponding properties of the oxidation products of the dyes;<sup>2</sup> this enabled most of the products to be identified. The paper strips were cut in at the base so as to obtain narrower bands.<sup>3</sup> The samples were placed on the starting line over the whole width of the paper (not in spots). The sizes of the strips were: length 20 cm.; width 2.5 cm.; width at the base 2.0 cm. Ascending development over 15 cm. was used.

$R_F$  values of some anthraquinone and naphthaquinone derivatives are given in Table 1. The bands can be fixed on the chromatograms by spraying with methanolic magnesium acetate, anthraquinone derivatives being converted into insoluble lakes with different colours.<sup>4</sup>

The results of the chromatographic and spectrophotometric comparisons are given in Table 2.

The first relatively stable product from 3-nitroalizarin had the same  $R_F$  values (in different eluants) and the same absorption spectrum as had 4-methoxy-3-nitroalizarin. On evaporating several partly faded solutions (SP 500 w lamp) and crystallising the residue from acetic acid a small amount of the product was isolated that after recrystallisation had m. p. 199—200°, not depressed on admixture with 4-methoxy-3-nitroalizarin (m. p. 203—204°).

Irradiated solutions of 3-nitroalizarin, 3-nitropurpurin, 4-methoxy-3-nitroalizarin, the acetal (II; for this and other formula numbers see the preceding paper), and the nitroacetyl quinone (III) also contained the glyoxylate (IV) as shown in Table 2. Chromatograms of the compounds present in partly faded solutions of 3-nitroalizarin and 4-methoxy-3-nitroalizarin also showed bands with  $R_F$  values approximately equal to those of the acetal (II) but the isolated products could not be sufficiently purified by repeated chromatography for satisfactory comparison of the absorption spectra.

Fading of the acetal (II) under the HP 125 w lamp and in sunlight gave the nitroacetyl-quinone (III) which could be isolated in sufficient quantity for crystallisation from methanol, after which it had m. p. and mixed m. p. 164—166°.

From partly faded solutions of the glyoxylate (IV) 2-hydroxy-1,4-naphthaquinone was isolated and identified. The same substance appeared to be present in all the faded solutions recorded in Table 2.

Absorption spectra of the isolated products and of the corresponding synthetic compounds are given in the Figures. As the concentration of the fading products identical with 4-methoxy-3-nitroalizarin was unknown, an arbitrary constant was added to  $\log \log (I_0/I)$  to make this

<sup>2</sup> Van Beek, Thesis, Delft, 1960.

<sup>3</sup> Matthias, *Naturwiss.*, 1954, **41**, 17.

<sup>4</sup> Shibata, Takito, and Tanaka, *J. Amer. Chem. Soc.*, 1950, **72**, 2789.

TABLE 1.

 $R_F$  values of some anthraquinone and naphthaquinone derivatives.

Substance *	$R_F$ on development with solvent †			Colour	Colour with Mg(OAc) <sub>2</sub>
	A	B	C		
Alizarin .....	0.88	0.41 ‡	0.64	Yellow	Violet
3-Nitroalizarin .....	0.68	0.30 ‡	0.35 ‡	Orange	Orange
3-Nitropurpurin .....	0.70	0.39	0.42	Red	Red
3-Aminoalizarin .....	0.71	—	—	Yellow	Blue
1,2,3-Trihydroxyanthraquinone .....	0.80	—	—	Yellow	Blue
Purpurin .....	—	0.27 ‡	0.60	Red	Red
1-Hydroxyanthraquinone .....	0.84	—	—	Yellow	—
2- " " .....	0.76	—	—	Yellow	—
Quinizarin .....	0.73	0.35 ‡	0.64	Yellow	Violet
4-Methoxy-3-nitroalizarin <sup>1,2</sup> .....	0.87	0.37 ‡	0.64	Orange	Red
Acetal (II) <sup>1,2</sup> .....	1.0	0.92	0.78	Yellow	Yellow
Nitroacetylquinone (III) <sup>1,2</sup> .....	1.0	0.70	0.61	Yellow	Yellow
Glyoxylate (IV) <sup>1,2</sup> .....	1.0	0.75	0.68	Yellow	Yellow
2-Hydroxy-1,4-naphthaquinone .....	0.89	0.70	0.73	Orange	Orange

TABLE 2.

Chromatography and spectrophotometry of fading products and of some oxidaton products of 3-nitro-alizarin and -purpurin

Expt. no.	Irradn. condns.	Wt. of substance (mmole)	Vol. of solvent (ml.)	Fading product		Synthetic product	
				$R_F$ †	$\lambda_{max.}$ (m $\mu$ )	$R_F$ †	$\lambda_{max.}$ (m $\mu$ )
<b>3-Nitroalizarin</b>				<b>4-Methoxy-3-nitroalizarin</b>			
1	SP 500 w, 24 hr., 32—36°	0.35	1000	0.85 A, 0.64 C	255—256, 420—425	0.85 A, 0.64 C	224—225, 256—257, 420—425
2	Sun, 7 days	0.11	50	0.85 A, 0.63 C	255, 420—435	"	"
3	SP 500 w, 80 hr., 32—36°	1.75	1000	0.95 B,** C	—	0.92 B, 0.77 C	Acetal (II) 271—272
<b>4-Methoxy-3-nitroalizarin</b>							
4	SP 500 w, 30 hr., 32—36°	0.32	1000	0.88—1.00 B, 0.77 C	—	0.88 B, 0.78 C	"
5	Sun, 7 days	0.095	50	0.88 B, 0.77 C	272—274	"	"
<b>3-Nitropurpurin</b>							
6	HP 125 w, 72 hr., 53—55°	0.10	30	0.85—1.00 B,** C	—	"	"
<b>3-Nitroalizarin</b>				<b>Glyoxylate (IV)</b>			
7	SP 500 w, 80 hr., 32—36°	1.75	1000	0.74 B, 0.69 C	271—273	0.75 B, 0.68 C	273—274
8	Sun, 14 days	0.11	50	0.73 B, 0.71 C	273	0.74 B, 0.70 C	"
<b>4-Methoxy-3-nitroalizarin</b>							
9	SP 500 w, 30 hr., 32—36°	0.32	1000	0.75 B, 0.68 C	273	0.75 B, 0.69 C	"
10	Sun, 7 days	0.095	50	0.74 B, 0.69 C	273	0.75 B, 0.68 C	"
<b>3-Nitropurpurin</b>							
11	HP 125 w, 72 hr., 53—55°	0.10	30	0.75 B, 0.69 C	272	0.75 B, 0.69 C	"
12	Sun, 14 days	0.10	50	0.75 B, 0.70 C	272—274	0.74 B, 0.68 C	"
<b>Acetal (II)</b>							
13	HP 125 w, 48 hr., 25—27	0.21	30	0.78 B	272—273	0.78 B	"
14	Sun, 2 days	0.07	50	0.74 B, 0.68 C	273—274	0.75 B, 0.68 C	"
<b>Nitroacetylquinone (III)</b>							
15	HP 125 w, 50 hr., 25—27°	0.19	30	0.75 B	273—274	0.75 B	"
16	Sun, 1 day	0.19	50	0.74 B, 0.68 C	274—275	0.73 B, 0.67 C	"

\* For formulæ see preceding paper. † Solvents: A, C<sub>6</sub>H<sub>6</sub>-MeOH-AcOH-H<sub>2</sub>O 30 : 60 : 4 : 6; B, MeOH-H<sub>2</sub>O-AcOH 30 : 65 : 5; C, light petroleum (b. p. 80—100°)-AcOH-MeOH 10 : 2 : 88. ‡ Tailing. \*\* Deformation of band.

value equal to  $\log E$  of 4-methoxy-3-nitroalizarin at the wavelength of maximum absorption (255  $m\mu$ ). The glyoxylate (IV) was purified by paper chromatography and the solutions obtained were used directly for determination of the absorption spectrum without measurement

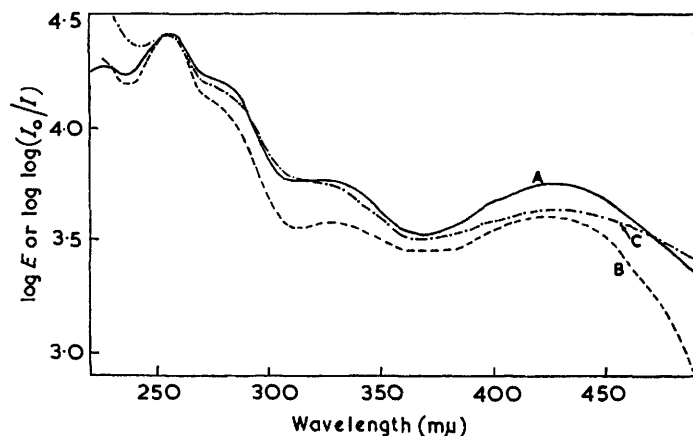


FIG. 1. Absorption spectra of (A) 4-methoxy-3-nitroalizarin, (B, C) fading product of 3-nitroalizarin (B, Hg-vapour lamps; C, sunlight).

FIG. 2. Absorption spectra of (—) methyl 3-hydroxy-1,4-naphthaquinon-2-ylglyoxylate (IV) and of the fading products (Hg-vapour lamps) of (· · ·) 3-nitroalizarin, (----) 3-nitropurpurin, (— · —) 4-methoxy-3-nitroalizarin, (○—○) the acetal (II), and (×—×) the nitroacetylquinone (III).

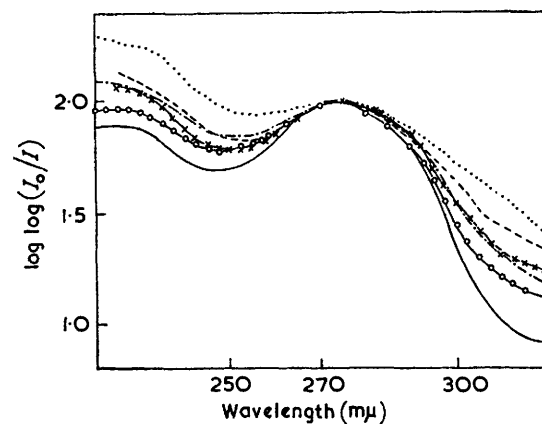
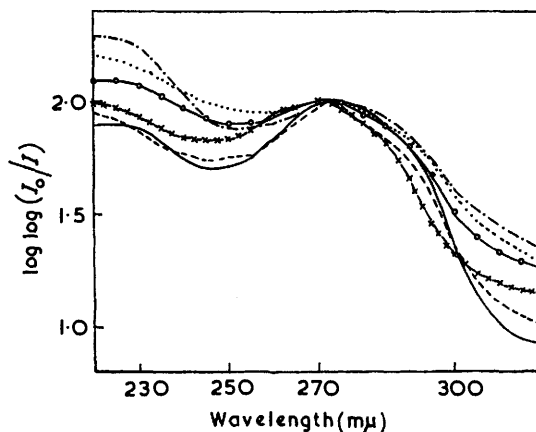


FIG. 3. Absorption spectra for fading in sunlight. Key as for Fig. 2.

of concentrations; therefore the values of  $\log \log (I_0/I)$  of the synthetic compound and of the fading products were arbitrarily fixed at 2.0 at the wavelength of maximum absorption (273—274  $m\mu$ ).

*Analysis of Completely Faded Solutions of 3-Nitro-alizarin and -purpurin and Some of Their*

*Oxidation Products.*—Prolonged exposure of 3-nitro-alizarin and -purpurin in methanol affords colourless end-products consisting mainly of organic acids.

Completely faded solutions (HP 125 w lamp) of 3-nitro-alizarin and -purpurin and of their chemical oxidation products were concentrated and the residues were boiled for a short time with dilute hydrochloric acid to hydrolyse esters of the organic acids, then placed on paper strips (12 × 40 cm.) in round spots. Descending development was used, for solvent G 25—35 cm., and for solvents E and F 15—25 cm. The temperature was kept at 23—25°. Solutions of known acids were run simultaneously. Some results are given in Table 3 (values in each row from one chromatogram).

TABLE 3.  
Chromatographic analysis of end-products.

Expt. no.	Substance irradiated	Solvent *	$R_F$ of acid products				$R_F$ of acids:		
							oxalic	phthalic	salicylic
1	3-Nitroalizarin .....	G	0.26	0.72		0.82	0.28	0.67	0.84
2	" .....	F	0.04	0.22		0.52	0.04	0.25	0.50
3	3-Nitropurpurin ...	G	0.27	0.68		—	0.28	0.70	—
4	" .....	E	0.19	0.35	0.49 †	0.60	0.18	0.34	0.61
5	4-Methoxy-3-nitro-alizarin .....	G	0.28	0.73		0.80	0.28	0.70	0.83
6	" .....	E	0.27	0.35 †	0.44	0.62	0.26	0.43	0.64
7	Acetal (II) .....	G	0.32	0.78		0.87	0.30	0.74	0.88
8	" .....	E	0.15	0.33		0.54	0.15	0.30	0.51
9	" .....	F	0.00	0.08	0.22 †	0.40	0.00	0.10	0.48
10	Nitroacetylquinone (III) .....	G	0.22	0.64		0.81	0.27	0.71	0.83
11	" .....	F	0.00	0.09		0.42	0.00	0.11	0.48
12	Glyoxylate (IV) ...	G	0.38	0.76		0.85	0.40	0.77	0.87
13	" .....	E	0.14	0.33		0.52	0.15	0.30	0.51
14	" .....	F	0.00	0.08	0.25 †	0.45	0.00	0.10	0.48

\* Solvents: E, EtOH-aq.  $\text{NH}_3$  ( $d$  0.94) 99.5 : 0.5; F, EtOH-aq.  $\text{NH}_3$  ( $d$  0.94) 99.9 : 0.1; G, PhOH- $\text{H}_2\text{O}$ -85%  $\text{H}\cdot\text{CO}_2\text{H}$  80 : 18 : 2. † Unidentified.

The completely faded solutions contained relatively large amounts of formaldehyde (colour reaction with chromotropic acid and sulphuric acid). From a faded solution of 4-methoxy-3-nitroalizarin phthalic acid was isolated and identified. The colour reaction with resorcinol and sulphuric acid was positive in samples from the faded solutions of all the compounds listed in Table 3. The chromatographic analysis was disturbed by the presence of relatively large amounts of formaldehyde, so that the  $R_F$  values obtained were not reproducible. Nevertheless strong indications were obtained for the presence of oxalic, phthalic, and salicylic acid in the faded solutions.

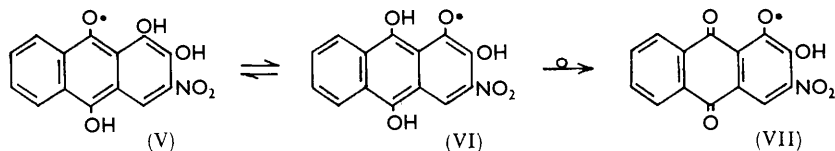
## DISCUSSION

From the analysis of partly faded solutions it can be concluded that 4-methoxy-3-nitroalizarin (I) and methyl 3-hydroxy-1,4-naphthaquinon-2-ylglyoxylate (IV) are formed by photochemical degradation of 3-nitroalizarin in methanol. The latter product is also formed on fading of 3-nitropurpurin, the acetal (II), and the nitroacetylquinone (III). Formation of the acetal on fading of 3-nitroalizarin and 4-methoxy-3-nitroalizarin was strongly indicated but not definitely proved. The nitroacetylquinone (III) could not be isolated from the partly faded solutions of 3-nitroalizarin, 3-nitropurpurin, or 4-methoxy-3-nitroalizarin, probably because of its sensitivity to light: fading of this compound is about 7 times as fast as that of 4-methoxy-3-nitroalizarin, so that its concentration in faded solutions is very low. However, it is rapidly formed on irradiation of the acetal (II).

Despite these imperfections the evidence warrants the conclusion that photochemical degradation of 3-nitroalizarin and 3-nitropurpurin follows the same course as the chemical degradations discussed in detail in the preceding paper.

The formation of oxalic, phthalic, and salicylic acid on prolonged photochemical degradation of 3-nitro-alizarin and -purpurin and their oxidation products also indicates parallelism between chemical and photochemical oxidation.

The results regarding the first in the photochemical degradation of nitroalizarin are in agreement with and amplify recent work on the photochemical oxidation of alcohols in the presence of anthraquinone dyes<sup>5</sup> where it was shown that a primary reaction was activation of the dyes to a singlet level followed by reaction with the substrate to form semiquinone radicals. The semiquinone radical of 3-nitroalizarin can be present in various



tautomeric structures and one of these (VI) can react with atmospheric oxygen to form the 9,10-quinone (VII) which by disproportionation can afford an anthra-1,2,9,10-diquinone capable of reacting with methanol to form 4-methoxy-3-nitroalizarin. It is probable that the photochemical degradation of 4-methoxy-3-nitroalizarin and 3-nitropurpurin proceeds in an analogous way. On chemical oxidation the diquinones are formed directly and give the same products.

Qualitatively, the same results were obtained by using sunlight or light from mercury-vapour lamps. Also changes of temperature between 20° and 55° did not appreciably change the course of the reactions.

Finally, fading of boiling solutions of 3-nitroalizarin and 3-nitropurpurin affords different products, as shown by chromatography, but their nature is not yet known.

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<sup>5</sup> Bolland and Cooper, *Proc. Roy. Soc.*, 1954, *A*, **225**, 405; Wells, *Nature*, 1956, **177**, 483; Bridge and Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 275; Bridge and Maclean, *J. Soc. Dyers Colourists*, 1959, **75**, 147.