680. *Fading and Tendering Activity in Anthraquinonoid Vat Dyes. Part V.*[1] *Photo-dehalogenation and -oxidation of* leuco-*Solutions.*

By C. J. COOPER and H. I. STONEHILL.

leuco-Solutions of the halogenated dyes Cibanone Brilliant Orange GK and Gold Yellow RK, and Caledon Brilliant Orange 6R, Orange 2RTS, and Brilliant Orange 4RN undergo rapid dehalogenation when exposed to visible light. In the presence of excess of dithionite dehalogenation is complete, but in catalytically prepared *leuco*-solutions with no excess of reductant dehalogenation proceeds to the extent of statistically one halogen atom per molecule, which releases sufficient oxidant to oxidise completely and thus precipitate all the *leuco*-dye present. Thus a dye containing *n* halogen atoms per molecule can undergo *n* successive reduction–irradiation–precipitation cycles. Potentiometric determinations show that not all the halogen liberated appears as halide ion; some is probably lost by adsorption on precipitated dye. Examination of the irradiation products by chromatography, *X*-ray diffraction, and conventional and differential absorption spectroscopy confirms the dehalogenation, and indicates that no monohalogenated product is formed from either di- or tri-halogenated dyes. The occasional production, under severe reducing conditions, of a *leuco*-solution which was not rapidly precipitated on irradiation, an effect enhanced by pyridine, is ascribed to the formation of tautomeric oxanthranol. The visible and ultraviolet absorption spectra of the catalytically prepared *leuco*-solutions of the above five dyes and nine others were determined, and by irradiation in the spectrophotometer the spectral region responsible for photo-dehalogenation was located as approximately 450—650 mμ for all five dyes concerned.

DURING preliminary work on the polarographic oxidation of *leuco*-Caledon Orange 2RTS,[1] difficulty was experienced in obtaining reproducible wave-heights. Since neither a rise in temperature from 25° to 50°, nor replacement of 48% aqueous ethanol as solvent by 50% aqueous pyridine, as used by Appleton and Geake[2] for potentiometric titrations, decreased the variability, the latter was not caused by precipitation of *leuco*-dye on cooling from the reduction temperature to 25°. It was traced to the action of light on the *leuco*-solution. When a thin layer of the purple *leuco*-solution in the capillary tube connecting the reduction vessel and the polarographic cell was illuminated by a 60-watt lamp a few inches from it, the liquid became colourless within a few minutes and a yellow precipitate appeared. In the dark, no fading or precipitation occurred after 1 hr., and polarographic wave-heights were reproducible and proportional to concentration. Hence subsequent polarograms were obtained in the dark.

Since precipitation was observed only if the *leuco*-solution was illuminated after removal from contact with the reduction catalyst, it was apparently due to oxidation, which would occur only in the absence of a reductant. Accordingly, the following rapid test was used to select those dyes among the 39 listed by Moran and Stonehill[3] which behaved like Caledon Orange 2RTS. An aqueous suspension of the dye was reduced with the minimum quantity of alkaline sodium dithionite solution, and equal volumes of the resulting *leuco*-solution were placed in two test-tubes. The surface of each solution was quickly covered with liquid paraffin to exclude air, and 1 ml. of 40% aqueous formaldehyde was added by means of a pipette below the oil layer, destroying excess of dithionite. One tube was immediately placed in a dark cupboard, and the other illuminated with a 100-watt electric lamp a few inches away. The extent of dye precipitation in the tubes was periodically

[1] Part IV, Cooper and Stonehill, preceding paper.
[2] Appleton and Geake, *Trans. Faraday Soc.*, 1941, **37**, 45, 60.
[3] Moran and Stonehill, *J.*, 1957, 765.

compared. The test was not completely reliable, especially for detecting slight photo-oxidation, since the crude method of excluding air permitted slight atmospheric oxidation. However, it showed clearly that only the five dyes named in the summary were strongly active, and examination under rigorous anaerobic conditions of catalytically prepared *leuco*-solutions [1] confirmed that these dyes alone underwent photoprecipitation.

All five active dyes are halogenated. The reported lability of halogen atoms, in certain vat dyes, to high vatting temperatures [4] and sunlight [5] suggests dehalogenation as a likely explanation of the photo-oxidation activity. Bradley [6] found that alkali replaced the halogen of dibromoanthanthrones by hydroxyl. This would not, however, provide oxidant which is necessary to account for the photo-oxidation and precipitation in the *leuco*-solutions. The replacement of halogen by hydrogen, on the other hand, provides the necessary oxidant, as shown by the purely stoicheiometric reaction
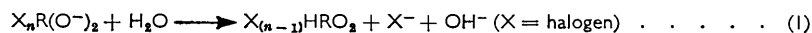
$$X_nR(O^-)_2 + H_2O \longrightarrow X_{(n-1)}HRO_2 + X^- + OH^- \quad (X = \text{halogen}) \quad . \quad . \quad . \quad . \quad (1)$$

Photo-induced exchange of halogen for hydrogen was reported by Goldstein and Gardner [7] for monohalogenated anthraquinols in visible light; they found α- more labile than β-halogen, and bromine more so than chlorine. In the highly alkaline *leuco*-solutions concerned here, the hydrogen substituent cannot be provided by hydrogen ions, and must presumably come from water molecules, as in reaction (1). Since replacement of only one halogen atom per molecule by hydrogen is sufficient to oxidise the *leuco*-dye completely, a dye with n halogen atoms per molecule should be photoactive for n successive cycles of reduction and exhaustive irradiation. This was verified for dyes with $n = 2$ and 3. No further activity was found after n cycles.

In order to obtain direct evidence of photo-dehalogenation, and to determine the amount of halide ion formed after each exhaustive irradiation, use was made of halide-ion concentration cells. The identity of the irradiation products was studied by comparing their absorption spectra and X-ray diffraction patterns with those of the original dyes and their unhalogenated analogues, and by using chromatographic separations and differential absorption spectroscopy. In connection with the spectrophotometric identification of the spectral region responsible for photo-dehalogenation of the *leuco*-dyes, the visible absorption spectra of their solutions were determined. The opportunity was taken to determine also their ultraviolet absorption spectra. To avoid errors due to ultraviolet absorption by the excess of dithionite used for reduction in previous work on the *leuco*-spectra,[3] the *leuco*-solutions were prepared by catalytic reduction.

EXPERIMENTAL

Materials.—Dioxan (technical) was refluxed with concentrated hydrochloric acid, and distilled over sodium. Phenol was of " AnalaR " grade. Other materials were as described previously.[1, 3]

Preparation of Irradiation Products.—A quantity of halogenated dye, sufficient to give 50 ml. of approx. mM-*leuco*-solution, was catalytically reduced as previously described [1] for polarography, and passed into the polarographic cell from which the electrodes had been removed. It was irradiated by a 100-watt electric lamp a few inches away, and samples of the well-shaken resulting suspension were removed after precipitation was complete (usually within 5 min.). An attempt to prepare the product of two or more successive reduction–irradiation cycles without removing the dye sample from the apparatus or renewing the catalyst failed because of poisoning of the catalyst by traces of *leuco*-solution on it which underwent photo-dehalogenation–oxidation during irradiation. Palladised and platinised asbestos catalysts were far more severely poisoned than Raney nickel.

Determination of Bromide Ion Formed on Irradiation.—A 5 ml. portion of irradiated *leuco*-solution was filtered, after atmospheric oxidation if necessary to complete precipitation, and
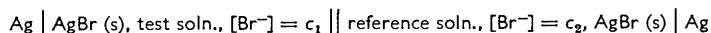
[4] Fox, *J. Soc. Dyers and Colourists*, 1949, **65**, 508.
[5] Weber, *Amer. Dyestuff Reporter*, 1933, **22**, 157.
[6] Bradley, *J. Soc. Dyers and Colourists*, 1954, **70**, 57.
[7] Goldstein and Gardner, *J. Amer. Chem. Soc.*, 1934, **56**, 2131.

combined with a reference potassium bromide solution (mM or 0·5mM) to form the concentration cell:

$$\text{Ag} \mid \text{AgBr (s), test soln., } [\text{Br}^-] = c_1 \parallel \text{reference soln., } [\text{Br}^-] = c_2, \text{AgBr (s)} \mid \text{Ag}$$

The E.M.F. (E mv) of this cell was measured at 25° with a Cambridge pH meter used as a valve potentiometer, and the value of c_1 calculated from the equation $E = 59 \log c_1/c_2$. The electrodes were silver-wire spirals coated electrolytically with silver bromide. They dipped into small beakers containing the appropriate solutions and connected by a salt-bridge tube fitted with ground-glass end-stoppers. To minimise junction potentials, test, bridge, and reference solutions contained the same high concentration of indifferent electrolyte as carrier solution. Since the *leuco*-solutions contained 0·1N-sodium hydroxide and 48% ethanol, this was at first tried as carrier solution. However, it caused drifting potentials in cells with known potassium bromide concentrations for both electrode solutions, probably owing to the effect of alkali on the electrodes. Erratic behaviour persisted in these cells on neutralisation of the solutions with 2N-nitric acid from a micro-burette (to Methyl Orange), but disappeared on addition to the neutralised solutions of a little solid sodium hydrogen carbonate as buffering agent. The test cell then gave reproducible non-drifting E values in accordance with the above equation. All cell solutions were thereafter treated similarly.

Absorption Spectra.—The precipitated irradiation product of each active *leuco*-solution was extracted from its suspension in alkaline aqueous ethanol with warm chlorobenzene, the extract dried (CaO) and filtered into an absorption cell (usually of 4 cm. optical path), and its visible absorption spectrum determined with the Hilger Uvispek spectrophotometer, fitted with a glass prism. Concentration was not controlled. Comparison spectra of chlorobenzene solutions of the original halogenated dyes and of their unhalogenated analogues were also determined.

leuco-Solution spectra were determined in both the ultraviolet and the visible region with the Uvispek instrument, solutions being prepared in the dark as follows. A suitable quantity of standard dye suspension in 50% v/v aqueous ethanol containing 0·1N-sodium hydroxide was reduced at 55° for ½ hr. with hydrogen and palladium or partially deactivated Raney nickel in the apparatus previously described.[1] One batch of palladium catalyst caused dehalogenation during reduction, and was rejected; nickel catalyst which had not been deactivated caused dehalogenation and produced fluorescent solutions. Interposed between the reduction vessel and the polarographic cell was a 2 cm. quartz absorption cell, fitted with a latex-gasketed airtight cap bearing integral inlet and outlet tubes and fabricated from a single block of Perspex; these tubes were connected to the rest of the apparatus by short lengths of polyvinyl chloride tubing bearing screw clips. The solution was diluted in the apparatus with sufficient aqueous 0·1N-sodium hydroxide to reduce the ethanol concentration to 16% v/v, cooled, and filtered through glass wool into the absorption cell. When this was completely filled, the screw clips were closed, and the cell was detached from the assembly and, while still shielded from light, placed in the spectrophotometer. Despite the photo-activity of the *leuco*-solutions of halo-genated dyes, the extent of photo-reaction during the determination of absorption spectra was found to be negligible with the low-powered 8-watt filament lamp light source of the Uvispek instrument, provided the maker's recommended slit widths for a 5 Å band-width were used with minimal exposure of the solutions. With a solution of the same composition, apart from omission of dye, as reference, the absorption spectra frequently exhibited a sharp maximum near 235 mμ, the intensity of which varied with the duration and temperature of reduction but was practically independent of dye or ethanol concentration, the nature of the alkali used, and the presence or absence of hydrogen or air in the reference solution. This may be either a spurious maximum [8] due to strong absorption by ethanol and sodium hydroxide in this spectral region, or else the absorption band of material extracted from the polyvinyl chloride tubing by the aqueous ethanol; the material extracted with 90% aqueous methanol has an absorption band at 225 mμ.[9] By using as reference solution a sample of the *leuco*-solution which was air-oxidised and filtered through glass wool after any colloidal dye had coagulated (15 min.), the optical density of this maximum was reduced to about 0·3; with the high concentrations of dye used, its effect on the position of dye absorption maxima in the 240 mμ region is probably small.

Identification of Spectral Region causing Photo-dehalogenation.—Each active *leuco*-solution,

[8] Bayliss and Brackenbridge, *Chem. and Ind.*, 1955, 477.
[9] Banks, Fazakerley, Keay, and Smith, *ibid.*, 1957, 1013.

prepared as described above, was irradiated for ½ hr. in the Uvispek apparatus with light from a 36-watt filament lamp source in a 25 Å band (obtained by widening the instrument slit width) centred on each in turn of the visible absorption maxima, and the optical density was measured before and after each irradiation. When a decrease in optical density occurred, the contents of the absorption cell were mixed by shaking before further irradiation. The active spectral region having thus been approximately located, further ½ hr. irradiations were performed with 25 Å band widths in neighbouring spectral regions to determine the limits of the active region; these were confirmed with fresh *leuco*-solution. Spectral regions causing no decrease in optical density after ½ hour's exposure were still without effect after exposure for 2 hr.

X-Ray Diffraction Powder Photographs.—Samples of Caledon Brilliant Orange 6R, its final product after two reduction–irradiation cycles, and its unbrominated analogue anthanthrone were recrystallised from chlorobenzene, and their *X*-ray powder diffraction photographs obtained by means of a Phillips *X*-ray diffraction apparatus, type 11704, fitted with a 11·46 cm. Debye–Scherrer powder camera.

Chromatographic Procedures.—Ascending filter-paper chromatograms of the irradiation products of active *leuco*-dyes, and of reference dyes and mixtures thereof, were obtained by impregnating one end of 12 in. × 1 in. paper strips with the appropriate dithionite-reduced *leuco*-solution, allowing air-oxidation to occur, washing out inorganic materials with water, drying, and suspending the paper overnight in gas jars with the impregnated lower end dipping into chlorobenzene. The constituents of the first irradiation product of the active dibrominated dye Caledon Brilliant Orange 6R were separated by column chromatography; a solution in chlorobenzene was poured on a 24 in. × 1 in. alumina column and developed with chlorobenzene until the yellow band was separated from the immobile narrow orange band; portions of the latter zone and each end of the extended yellow band were extracted with chlorobenzene, and the visible absorption spectra of the extracts plotted.

RESULTS AND DISCUSSION

(i) *Bromide Ion Liberated on Irradiation of* leuco-*Solutions.*—Caledon Brilliant Orange 6R, a dibromo-dye, was reduced at 80° for 1 hr. in 48% v/v aqueous ethanol containing 0·1N-sodium hydroxide. The bromide ion liberated after various numbers of reduction–irradiation cycles is given in Table 1. To establish whether this release of bromine

TABLE 1.

Dye concn. (mM)	0·42	0·862	0·862	0·862	0·862
No. of cycles	4	1	3	1	3
Br⁻ liberated (ions/dye mol.)	1·05	0·75	1·40	0·40	0·96

occurs on irradiation or merely on reduction, the bromide concentration was determined in a portion of 0·862mM-*leuco*-solution after air-oxidation in the dark. The result, approximately 0·02 Br⁻ ion per dye molecule, indicates that virtually no dehalogenation of dye occurs in the absence of irradiation.

The amount of bromide ion released in these experiments is much less than that according to reaction (1), namely, one ion per dye molecule for each of the first two irradiations. Similar low yields of bromide (see Table 2) were obtained with 0·774mM-

TABLE 2.

Run		A			B			C	
No. of irradiations	1	2	3	1	2	1	2	3
Br⁻ liberated (ions/dye mol.)...	0·22	0·48	0·62	0·16	0·29	0·11	0·16	0·26

TABLE 3.

Solvent	48% pyridine		48% pyridine		48% dioxan		48% EtOH + 0·01M-PhOH
No. of irradiations	1	2	1	3	1	3	1
Br⁻ liberated (ions/dye mol.) ...	0·96	1·65	0·85	1·23	0·82	1·36	0·76

leuco-solutions of Caledon Brilliant Orange 4RN, the only trihalogenated dye available, prepared in the same way. This suggests that some of the bromide ion is removed from

solution by entrainment in, or adsorption on, the precipitated quinones. The limited data available are in fact consistent with a Freundlich-type adsorption isotherm.

The alternative possibility, suggested by the ester-like odour of irradiated solutions, that some of the liberated bromine atoms were removed by reaction with the ethanol to become covalently bound, is not only energetically improbable,[10] but is not supported by the results obtained (Table 3) on irradiating 0·862mM-*leuco*-Caledon Brilliant Orange 6R in 48% aqueous pyridine or dioxan, which are brominated less readily than ethanol, and in 48% aqueous ethanol containing phenol, which reacts readily with bromine atoms. In fact, bromide recovery is not significantly different with the various solvents used, and may approach the theoretical value for the first irradiation quite closely. Precipitation during irradiation was noticeably slower in pyridine than in ethanol, and on completion left a slightly coloured supernatant solution, whereas with ethanol the latter was colourless (cf. section iv). When the precipitate from an irradiated pyridine solution was filtered off and the filter-paper allowed to dry in air, the paper had an odour suggesting the presence of acetamide; this might indicate some attack on the pyridine, since it was not observed unless the photo-reaction had occurred.

(ii) *Identification of Final Irradiation Products.*—The absorption spectra of chlorobenzene solutions of various active halogenated dyes, their successive reduction–irradiation products, and the corresponding inactive unhalogenated dyes were determined in the visible region. Absorption peak wavelengths are given in Table 4, and a complete set

TABLE 4. *Absorption maxima for active dyes, their irradiation products, and their unhalogenated analogues.*

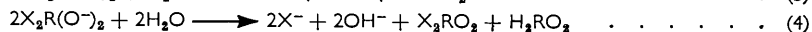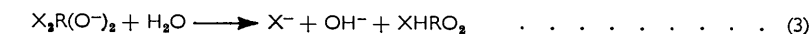| Dye	No. of halogen atoms in mol.	No. of irradiations	$\lambda_{max.}$ (mμ)		
Caledon Brilliant Orange 6R	2	0	492	462	—
		1	484	456	—
		2	478	450	—
Cibanone Brilliant Orange GK	2	0	492	465	—
		1	484	458	—
		2	478	450	—
Anthanthrone	0	0	478	450	—
Caledon Orange 2RTS	2	0	488	456	435
		1	482	450	431 *a*
		2	474	443	424 *a*
Caledon Brilliant Orange 4RN	3	0	496	465	435
		1	491	461	435
		2	483	450	430 *a*
		3	474	444	423 *a*
Caledon Gold Orange G	0	0	474	443	424 *a*
Cibanone Golden Yellow RK	2	0	473	443	420
		1	469	440	415
		2	466	436	410
Cibanone Golden Yellow GK	0	0	466	436	410

a Inflection.

of spectra for the representative dye Caledon Brilliant Orange 4RN in Fig. 1. The absorption maxima of successive irradiation products show a progressive bathochromic shift until, after as many irradiations as there are halogen atoms in the dye molecule, they coincide with those of the analogous unhalogenated dyes.

Confirmation of the identity of the final irradiation product of Caledon Brilliant Orange 6R and the unhalogenated analogue anthanthrone was obtained from a comparison of their X-ray powder diffraction patterns.

(iii) *Identification of Intermediate Irradiation Products.*—Reaction (1) requires the loss of statistically one halogen (X) atom per dye molecule. For a dihalogenated dye, this

[10] Walling, " Free Radicals in Solution," John Wiley & Sons, Inc., New York, 1957, p. 370.

could occur either by all the dye molecules losing one, or half the dye molecules losing both halogen atoms:

$$X_2R(O^-)_2 + H_2O \longrightarrow X^- + OH^- + XHRO_2 \qquad \cdots \cdots \cdots \quad (3)$$

$$2X_2R(O^-)_2 + 2H_2O \longrightarrow 2X^- + 2OH^- + X_2RO_2 + H_2RO_2 \quad \cdots \cdots \quad (4)$$

Since the absorption peaks are broadened for the intermediate irradiation products (Fig. 1), the latter would appear to be mixtures. To decide this, paper-strip ascending chromatograms were obtained for (*a*) Caledon Brilliant Orange 6R, (*b*) its first reduction–irradiation product, (*c*) the unhalogenated analogue anthanthrone, and (*d*) an equimolar mixture of (*a*) and (*c*). For (*a*),·a narrow undevelopable orange band was obtained; for (*c*), a broad developable yellow band; for both (*b*) and (*d*), both these bands. A larger quantity of (*b*) was separated chromatographically on an alumina column: the orange and the yellow fraction gave absorption spectra identical respectively with those of (*a*) and (*c*). Thus the first photo-dehalogenation proceeds, as regards the products, according to reaction (4),

FIG. 1. *Spectra of* (*a*) *Caledon Brilliant Orange 4RN, and its* (*b*) *first,* (*c*) *second, and* (*d*) *third irradiation product, in* PhCl (4 *cm. cell*).
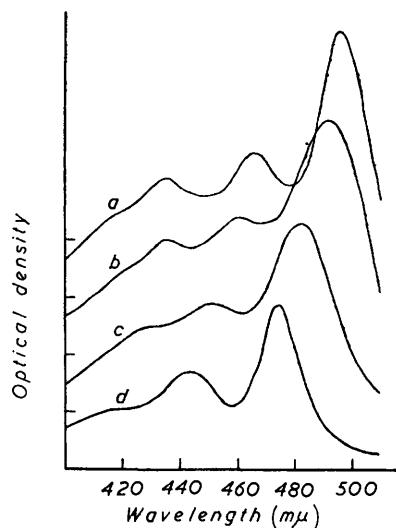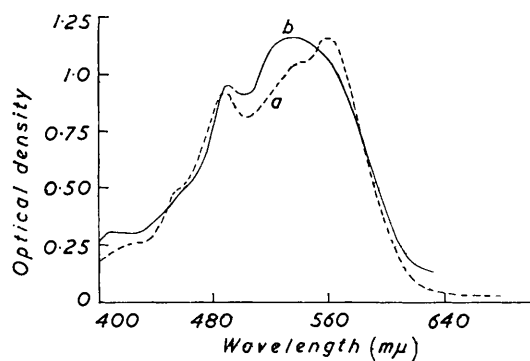

FIG. 2. *Absorption spectrum of leucoanthanthrone reduced at* (*a*) 55° *for* ¼ *hr. and* (*b*) 85° *for* 4 *hr., with hydrogen and palladium, in* 48% *aq.* EtOH + 0·1N-NaOH (2 *cm. cell length*).
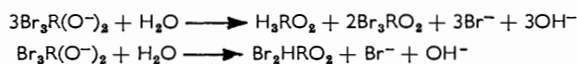

and there is no evidence of the formation of the monohalogenated dye. It is nevertheless more plausible to suppose (cf. section viii), that the initial dehalogenation product is the monohalogenated semiquinone or quinol. Some of this may be further dehalogenated and then oxidised to unhalogenated quinone, while the greater part must be assumed to undergo disproportionation to dihalogenated and unhalogenated analogues, either in solution as quinol or semiquinone, or after precipitation as quinone, probably upon redissolution, *e.g.*, in chlorobenzene for spectral examination. The original quinone precipitate might then consist of mixed crystals of molecules containing 0, 1, and 2 halogen atoms. In this connection it is of interest that the first irradiation product of Caledon Brilliant Orange 6R gave an *X*-ray powder diffraction pattern different from that of an equimolar mixture of the original dye and anthanthrone, the difference being largely removed by recrystallisation of the product from chlorobenzene.

Further examination of the first irradiation product of dihalogenated dyes was made by differential absorption spectroscopy. The visible absorption spectrum in chlorobenzene was determined with a chlorobenzene solution of the original dye in the reference cell, the concentration of the latter solution being adjusted to match that of the original dye in the test solution by diluting with solvent until the optical densities balanced at a wavelength

at which the original dye, but not its unhalogenated analogue, absorbs appreciably; this is possible because the halogenated dyes absorb at longer wavelengths than their unhalogenated analogues. The resulting differential absorption spectrum should be due entirely to solutes present other than the original dye. The technique was capable of indicating in 1 : 4 to 4 : 1 synthetic mixtures of halogenated and unhalogenated dyes both the presence and the approximate concentration ratio of the latter constituents. For the first irradiation products of Caledon Brilliant Orange 6R, Caledon Brilliant Orange GK, Caledon Orange 2RTS, and Cibanone Golden Yellow RK, the absorption peak wavelengths of the differential spectra corresponded with those of the unhalogenated analogues, and the optical density corresponded to approximately equimolar amounts of the original dye and its unhalogenated analogue.

For the tribrominated dye Caledon Brilliant Orange 4RN we may suppose, by analogy, that the initial product of the first irradiation is a mixture of the semiquinones and quinols with 0—3 bromine atoms per molecule. Again the monobromo-quinol, -semiquinone, and -quinone must be presumed to undergo bromine disproportionation, so that eventually only the original dye, the dibromo-dye (Caledon Orange 2RTS), and the unbrominated analogue (Caledon Gold Orange G) are present. The differential absorption spectrum of the first irradiation product of the tribromo-dye (the original dye being used as reference) has peaks at 485, 454, and 433 mμ. Comparison with the peak wavelengths for the first irradiation product of Caledon Orange 2RTS (Table 4) suggests the presence of the latter dye together with rather less than an equimolar amount of Caledon Gold Orange G. The quantities of the tribromo-, dibromo-, and unbrominated dyes are finally estimated from peak intensities to be approximately in the molar ratios 4 : 3 : 2. This satisfies the stoicheiometric requirement of statistical loss of one bromine atom per dye molecule, as in either of the processes

$$3Br_3R(O^-)_2 + H_2O \longrightarrow H_3RO_2 + 2Br_3RO_2 + 3Br^- + 3OH^-$$

$$Br_3R(O^-)_2 + H_2O \longrightarrow Br_2HRO_2 + Br^- + OH^-$$

both of which, as regards the final products, must be assumed to occur.

(iv) *Oxanthranol Formation.*—The residual purple solution left after irradiating the *leuco*-solution of Caledon Brilliant Orange 6R in 48% aqueous pyridine was mentioned in section (i). With aqueous ethanol as solvent, this purple colour was only occasionally obtained. Whereas irradiation normally caused complete precipitation within 5 min., leaving a colourless liquid, the purple colour, when it occurred, persisted for up to 2 hr. under irradiation, fading gradually. Since certain anthraquinonoid *leuco*-dyes tautomerise to oxanthranols, especially when incompletely ionised,[11] $R(OH)_2 \rightleftharpoons O\colon RH\cdot OH$, it was of interest to find whether the occurrence of the purple solution and the failure to undergo rapid and complete precipitation in light were due to the formation during reduction of some oxanthranol, which slowly reverts to the quinol as the latter is removed during irradiation.

Since oxanthranol formation is enhanced by severe vatting conditions,[11] a preliminary investigation was made of the effect of varying the duration and temperature of vatting on the visible absorption spectrum of the *leuco*-solution obtained by catalytic reduction (palladised asbestos) in 48% aqueous ethanol containing 0·1N-sodium hydroxide, the unhalogenated dye anthanthrone being used in order to avoid complications from dehalogenation during vatting. The spectra obtained after vatting at (*a*) 55° for ½ hr. and (*b*) 85° for 4 hr. are shown in Fig. 2. Clearly, the severe conditions of (*b*) cause modifications of the spectrum, which may be due to enhanced oxanthranol formation.

Next, a 0·862mM-*leuco*-solution of Caledon Brilliant Orange 6R in the same solvent was prepared similarly under fairly severe conditions (1 hr. at 65—70°), cooled, irradiated for ½ hr. so that the supernatant liquid was only faintly purple, and filtered. Its visible absorption spectrum differed very greatly from that of the original *leuco*-solution. The filtered solution was then irradiated for a further 3 hr., a yellow precipitate being

[11] Coffey, *Chem. and Ind.*, 1953, 1068.

formed and the solution becoming colourless. The precipitate, which underwent no visible change on exposure to air, was extracted with chlorobenzene. Its visible absorption spectrum in this solvent was found to be identical with that of anthanthrone. This accords with the view that half of the solute in the purple solution was the dibromo-oxanthranol derived from the original dye, the other half being the oxanthranol, or less probably the quinol, derived from anthanthrone. Thus there is strong evidence of the formation of oxanthranol on vigorous vatting.

(v) leuco-*Dye Spectra.*—Wavelengths and molar extinction coefficients of absorption peaks in both the visible and the ultraviolet region are given in Table 5, although only the visible spectra were required in connection with the identification of the spectral regions causing photo-dehalogenation. Agreement with the earlier determinations of the visible spectra by Moran and Stonehill[1] is satisfactory, apart from a few minor discrepancies probably due to less effective prevention of atmospheric reoxidation in the earlier work.

(vi) *Absorption Bands causing Photo-dehalogenation.*—The upper and lower wavelength limits of the active bands and their means are listed in Table 6. The technique used is incapable without further refinement of determining the wavelengths for maximum activity, but it is significant that for each *leuco*-dye the mean of the extreme wavelengths corresponds approximately with a main absorption peak listed in Table 5. No activity was detected in the ultraviolet range available with the spectrophotometer.

TABLE 5. *Ultraviolet and visible absorption spectra of* leuco-*dyes.*

Results are for $c \times 10^{-5}$M-solutions in 16% aqueous ethanol containing 0·1N-sodium hydroxide, in 2 cm. cells. Italics indicate an inflection.

Dye	c	$\lambda_{max.}$ (mμ)/log ε
Algol Yellow WG	4·0	234/3·96, 279/4·25, *302/4·08, 405/3·84,* 423/4·00, 535/3·79
Caledon Red X5BS	5·0	243/4·11, 286/4·19, *300/4·13, 335/3·81, 417/3·68,* 436/3·79, 558/3·72
Caledon Red 5G	4·0	234/4·13, 275/4·29, 327/3·83, *343/3·76, 394/3·70,* 411/3·81, 431/3·76, 494/3·70, 560/3·49
Anthanthrone	5·0	243/4·22, 256/4·23, 316/4·26, *430/3·34, 458/3·66,* 487/3·98, 535/4·03, 559/4·06
Cibanone Brilliant Orange GK	4·0	239/4·37, 261/4·35, 324/4·33, *465/3·72,* 493/3·96, *560/3·99,* 580/4·02
Caledon Brilliant Orange 6R	3·5	244/4·31, 261/4·32, 325/4·30, *464/3·69,* 493/3·93, *559/3·98.* 582/4·02
Caledon Gold Orange G	5·0	238/3·91, 256/3·92, 295/4·09, 308/4·10, *330/3·59, 345/3·42,* 390/3·15, *515/3·97,* 545/4·06
Caledon Orange 2RTS	7·5	243/3·91, 264/3·93, 301/4·12, 311/4·08, *350/3·40,* 390/3·11, *525/3·98,* 554/4·05
Caledon Brilliant Orange 4RN	6·5	246/3·81, 265/3·85, 307/4·07, *350/3·32,* 390/3·11, *530/3·96,* 559/4·03
Cibanone Golden Yellow GK	3·5	235/4·10, 272/4·00, *304/4·12,* 313/4·21, *456/3·82,* 479/3·97, 516/3·72, 554/3·69
Cibanone Golden Yellow RK	6·0	244/4·10, 276/4·09, 321/4·24, *464/3·86,* 488/4·05, *525/3·72,* 560/3·65
Cibanone Blue RSN	2·0	240/4·22, 300/4·32, 320/4·38, *360/3·72,* 550/3·60, 730/3·95
Caledon Blue RC	3·0	242/4·15, *304/4·25,* 323/4·46, *370/3·72,* 565/3·52, 770/4·15

(vii) *Photo-dehalogenation in the Presence of Excess of Reductant.*—Dilute suspensions of the photo-active dyes were reduced with excess sodium dithionite in 0·1N-aqueous sodium hydroxide, and the *leuco*-solutions were illuminated by a 100-watt electric lamp at a few inches distance for $\frac{1}{2}$ hr. Comparison with control solutions kept in the dark showed that irradiation caused a change of colour towards that of the corresponding unhalogenated *leuco*-dye solution. Both the controls and the irradiated solutions were then air-oxidised, and the visible absorption spectra of the precipitates were determined after extraction into chlorobenzene. In all cases the spectrum of the control coincided with that of the original dye, while that of the irradiated sample corresponded with that of the unhalogenated analogue, indicating complete dehalogenation.

(viii) *Mechanism of Photo-dehalogenation of* leuco-*Solutions.*—The above work leads to the following conclusions: (*a*) The rapidity of photo-dehalogenation implies that the
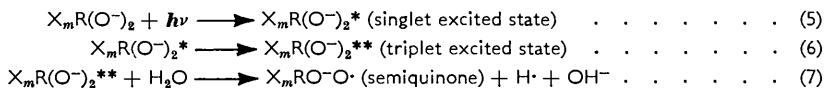
dye quinol rather than the semiquinone is the species primarily attacked, since the semi-quinone is present to only a very small extent, especially in the presence of excess of reductant. (*b*) Photo-oxidation of *leuco*-dye, which accompanies the dehalogenation if the reductant is not in excess, requires transfer of electrons from the dye to a reducible

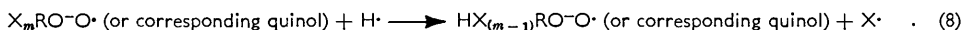TABLE 6. *Waveband responsible photo-dehalogenation.*

	Active wavelengths (mμ)		
Dye	Lower limit	Upper limit	Mean
Cibanone Brilliant Orange GK	460	650	555
Caledon Brilliant Orange 6R	460	650	555
Caledon Orange 2RTS	480	630	555
Caledon Brilliant Orange 4RN	450	670	560
Cibanone Golden Yellow RK	480	620	550

species; of those available, water is more probably involved than hydrogen ion in view of the high pH, especially in the hydration shell surrounding the dye molecule. (*c*) The halogen is liberated as free atoms, since a tribromo-dye yields some dibromo-dye on photo-dehalogenation. (*d*) Statistically one halogen atom per dye molecule is lost in a single exhaustive irradiation, but recovery of halide ion in solution may be less than corresponds to this because of adsorption on or entrainment with precipitated quinones. (*e*) Upon photo-dehalogenation a dihalogenated dye gives products with 0 and 2 halogen atoms per molecule, a trihalogenated dye products with 0, 2, and 3 halogen atoms per molecule; neither gives a monohalogenated product.

On the basis of conclusions (*a*)—(*d*), a mechanism for photo-oxidation–dehalogenation was proposed by Moran and Stonehill.[12] This requires some modifications in view of (*e*). It is now suggested that monohalogenated quinols and semiquinones are formed as inter-mediates, but are further dehalogenated by H· radicals or undergo disproportionation to dihalogenated and unhalogenated analogues in solution or after oxidation to quinones, especially when the latter are dissolved for recrystallisation or spectral examination. The modified reaction scheme is as follows, it being assumed that no excess of reductant is present, and $m = 2$ or 3.

$$X_mR(O^-)_2 + h\nu \longrightarrow X_mR(O^-)_2^* \text{ (singlet excited state)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$X_mR(O^-)_2^* \longrightarrow X_mR(O^-)_2^{**} \text{ (triplet excited state)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$X_mR(O^-)_2^{**} + H_2O \longrightarrow X_mRO^-O· \text{ (semiquinone)} + H· + OH^- \quad . \quad . \quad . \quad . \quad (7)$$

The H atom released per quinol molecule photo-oxidised to semiquinone displaces an equivalent of halogen atoms from any halogenated quinol or semiquinone, usually only one from any molecule, but occasionally 2 or, when possible, 3:

$$X_mRO^-O· \text{ (or corresponding quinol)} + H· \longrightarrow HX_{(m-1)}RO^-O· \text{ (or corresponding quinol)} + X· \quad . \quad (8)$$

Some $H_2X_{(m-2)}RO^-O·$, $H_mRO^-O·$, and the corresponding quinols are produced by repetition of process (8). When all the quinols have been completely photo-oxidised to semiquinones, the halogen atoms released are sufficient to oxidise all semiquinones to quinones:

$$H_nX_{(m-n)}RO^-O· + X· \longrightarrow H_nX_{(m-n)}RO_2 + X^- \quad (m \geqslant n \geqslant 0)$$

Disproportionation of any monohalogenated quinol, semiquinone, or quinone removes any monohalogenated quinol from the final product: $2H_{m-1}XR(O^-)_2$ (or corresponding semiquinone or quinone) $\longrightarrow M_mR(O^-)_2 + H_{(m-2)}X_2R(O^-)_2$ (or corresponding semiquinones or quinones).

In the presence of excess of reductant, *e.g.*, dithionite, reactions (5—8) are followed by reduction of X· to X$^-$ and of the semiquinones to quinols, which may then undergo the same reaction sequence until dehalogenation is complete.

[12] Moran and Stonehill, *J.*, 1957, 788.

4 T