679. *Fading and Tendering Activity in Anthraquinonoid Vat Dyes. Part IV.*[1] *Polarographic Oxidation of* leuco-*Dyes.*

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Polarographic oxidation of the *leuco*-solutions in 48% aqueous ethanol of 12 anthraquinonoid vat dyes, some of which exhibit fading and tendering activity, was studied at 25° at pH 11·15—12·88. Most of the dyes give adsorption waves. Three give a single diffusion wave corresponding to one-step oxidation of quinol to quinone. Four others give in addition another of different height, at more positive potentials, ascribed to bivalent oxidation of the tautomeric oxanthranol. Two others give two such additional waves, ascribed to bivalent oxidations of some anthrone and anthranol formed by over-reduction of the oxanthranol during vatting. The three remaining dyes give two diffusion waves of approximately equal height, probably due to bivalent oxidations of quinol and oxanthranol, as for four other dyes. Comparison with potentiometric data indicates that polarography is incapable of revealing the formation of relatively stable semiquinones by many of these dyes. There is no obvious relation between half-wave potentials for quinol oxidation and tendering activity, although more negative values tend to be associated with fading. Intense irradiation of the *leuco*-solutions in the region of the dropping-mercury electrode with visible light, even in the presence of potential mediators, or with *X*-rays, is without effect on the polarograms; this contrasts with the effect during potentiometric titration of tendering-active dyes.

Since fading and tendering phenomena are associated with oxidation or reduction of a photoactive dye,[1] the redox characteristics of the dye, in particular the stability of a semiquinone, may be involved in determining the efficiency of photosensitisation. Potentiometric examination of the redox characteristics of anthraquinonoid vat dyes is rendered difficult by their low solubility in water. Geake and his co-workers [2] determined the redox potentials and semiquinone formation constants of some of such dyes by potentiometric oxidative titration of their *leuco*-solutions in aqueous organic solvents, mainly

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[1] Part III, Moran and Stonehill, *J.*, 1957, 788.

[2] (*a*) Geake and Lemon, *Trans. Faraday Soc.*, 1938, **34**, 1409; (*b*) Appleton and Geake, *ibid.*, 1941, **37**, 45; (*c*) *Idem*, *ibid.*, p. 60.

50% pyridine. Gupta [3] and Marshall and Peters [4] similarly obtained the redox potentials of acid *leuco*-dyes in anhydrous pyridine, but in the absence of data on the dissociation constants of the *leuco*-acids, it is impossible to relate these potentials to those obtained in alkaline media. Waly, Preston, Scholefield, and Turner [5] carried out potentiometric redox titrations of aqueous suspensions of vat-dyed cotton, using potential mediators to ensure electrode equilibrium. They observed a constant potential during the major part of each titration, due to dye insolubility. For tendering dyes only, this constant potential was shifted to more negative values upon illumination; a similar but smaller shift occurred for aqueous suspensions of such dyes without cotton. Hadfield [6] could not reproduce these potential shifts, apart from a slight effect when traces of oxygen were present. Waly *et al.*[5] ascribed the shift to change in either the chemical nature or the solubility of the dye or its *leuco*-derivative. Turner [7] later suggested that the cause was a very active unidentified species produced during reduction of the dye.

The present paper describes an attempt to investigate the redox behaviour of some anthraquinonoid vat dyes by polarography, which has been used in a similar study of other types of dye [8] and of simple anthraquinone derivatives.[9] The possibility of a polarographic analogue of the potential shifts mentioned above was also investigated. During the work, photochemical dehalogenation of certain *leuco*-dyes was observed; the following paper records a study of this phenomenon.

Although anthraquinone has been polarographically reduced in solution in aqueous dioxan,[10] *NN*-diethylformamide,[11] and aqueous methanol,[12] as well as while solubilised in aqueous chloroform with wetting agents,[13] attempts to reduce polarographically Caledon Gold Orange G dissolved in anhydrous dioxan and pure or aqueous ethanol failed, essentially because of low dye-solubility. Attention was therefore confined to the polarographic oxidation of *leuco*-dyes in 48% aqueous ethanol, the ethanol being included to facilitate catalytic reduction of the dyes.

EXPERIMENTAL

Materials.—The dye samples were purified by Moran and Stonehill's method.[14] Algol Yellow WG (1-benzamidoanthraquinone) thus prepared was yellow-brown and gave abnormally small polarographic diffusion currents, suggesting the presence of an impurity. This dye was therefore synthesised from recrystallised 1-aminoanthraquinone at the lowest practicable temperature, washed with sodium hydroxide solution, water, and ethanol, and twice recrystallised from xylene (yellow needles). The anthanthrone used was a small commercial sample (Imperial Chemical Industries Limited, Dyestuffs Division), recrystallised from chlorobenzene. The dyes were used as standard 0·1% or 0·2% suspensions in 50% aqueous ethanol, prepared by grinding the dyes with water to a smooth paste with the aid of a palette knife and glazed tile, and then diluting them suitably.

Buffers were prepared from "AnalaR" carbonate-free sodium hydroxide, disodium hydrogen phosphate, and boric acid, with sufficient "AnalaR" potassium chloride to give a final ionic strength of 0·1. Their pH values in water and apparent pH values in 48% aqueous ethanol, determined with the Cambridge pH meter and "Alki" glass electrode, were:

Buffer	0·1N-NaOH	Phosphate	Phosphate	Borate
pH in water	12·70	11·80	10·93	10·13
pH in 48% ethanol	12·88	12·12	11·56	11·15

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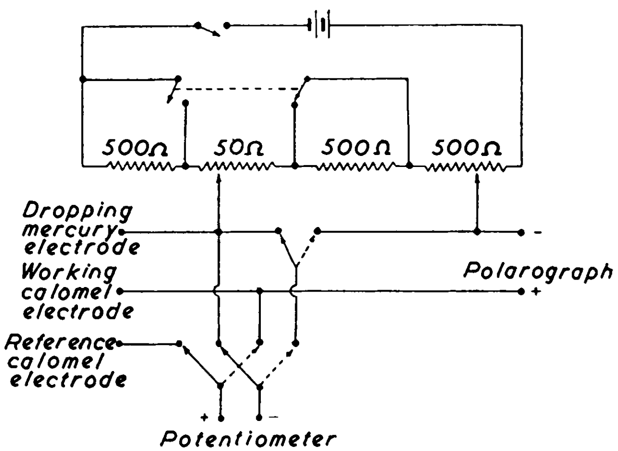
[3] Gupta, *J.*, 1952, 3479.
[4] Marshall and Peters, *J. Soc. Dyers and Colourists*, 1952, **68**, 289.
[5] Waly, Preston, Scholefield, and Turner, *ibid.*, 1945, **61**, 245.
[6] Hadfield, M.Sc. (Tech.) Thesis, Manchester, 1948.
[7] Turner, *J. Soc. Dyers and Colourists*, 1949, **65**, 637.
[8] Kaye and Stonehill, *J.*, (*a*) 1951, 27; (*b*) 1951, 2638; (*c*) 1952, 3231, 3244.
[9] Gill and Stonehill, *J.*, 1952, (*a*) 1845, (*b*) 1857.
[10] Furman and Stone, *J. Amer. Chem. Soc.*, 1948, **70**, 3055.
[11] Edsberg, Eichlin, and Garis, *Analyt. Chem.*, 1953, **25**, 798.
[12] Vainshtein, *Zavodskaya Lab.*, 1949, **15**, 411.
[13] Proske, *Analyt. Chem.*, 1952, **24**, 1834.
[14] Moran and Stonehill, *J.*, 1957, 765.

Sodium dithionite (Brotherton and Co. Ltd.) was of 98—99% purity. The ethanol was redistilled absolute alcohol. Mercury for polarography was treated with permanganate solution, sprayed through mercurous nitrate solution, washed with water, and vacuum-distilled three times. Raney nickel was prepared according to Vogel's directions[15] and stored under absolute alcohol. It retained its activity for several weeks, but then deteriorated rapidly. A suitable volume of the well-shaken suspension was pipetted out as required. Platinised and palladised asbestos (5%) were commercial samples. Hydrogen (from a cylinder) was rigorously deoxygenated by passage through a Baker Platinum "Deoxo" catalyst unit, followed by a Pyrex tube packed with palladised asbestos and heated to about 400° by a tubular electric heater. The "Deoxo" unit was at first used at room temperature, but in later work it was kept at about 100° by means of an Exothermal electric heating tape wound around it.

Apparatus.—Polarograms were obtained by means of a Tinsley Recording Polarograph, Model V 3211. Since the fixed voltage scanning speed of this instrument, 0·5 v/min., was too fast for accurate determination of wave-forms and potentials, it was reduced 5-fold by similarly reducing the potential across the polarograph potentiometer by means of a 1500-ohm 2-watt wire-wound series resistor in the battery circuit, this resistor being put out of circuit when normal scanning speed was desired. An additional effect of the resistor was the reduction of the potential span of the polarograph potentiometer from the normal range of +0·5 to −3·0 v, to the narrow range +0·1 to −0·6 v. In order to permit a wider span, an auxiliary voltage-dividing potentiometer was inserted between the polarograph and the cell to provide a biassing voltage. With this circuit, shown in Fig. 1, voltages within the ranges 0—1 or 1—2 could be tapped off, depending on which 500 ohm resistor were put out of circuit. Thus the polarographic potential span was 0·7 v situated anywhere between the limits +0·1 and −2·6 v. Voltages supplied by the polarograph together with the auxiliary potential divider were measured with a Pye Precision Potentiometer, which also served to determine the potential of the dropping-mercury electrode against a reference saturated calomel electrode carrying no current, in order to correct for ohmic potential drop across the cell.

FIG. 1.



Since the d. c. amplifier of the polarograph was unidirectional in operation, a large counter-current zero correction was required when the polarograph was used for oxidative (anodic) polarography and the applied voltage sweep was in the normal direction, towards increasingly negative values, in order that the polarographic zero current should correspond to maximum recorder-galvanometer deflection. Under these conditions the recorder deflection was no longer linearly related to cell current, as it was when zero cell current corresponded to only a small recorder deflection. To overcome this difficulty, the polarity of the polarograph potentiometer was reversed for oxidative polarography, as were the cell electrode connections. This

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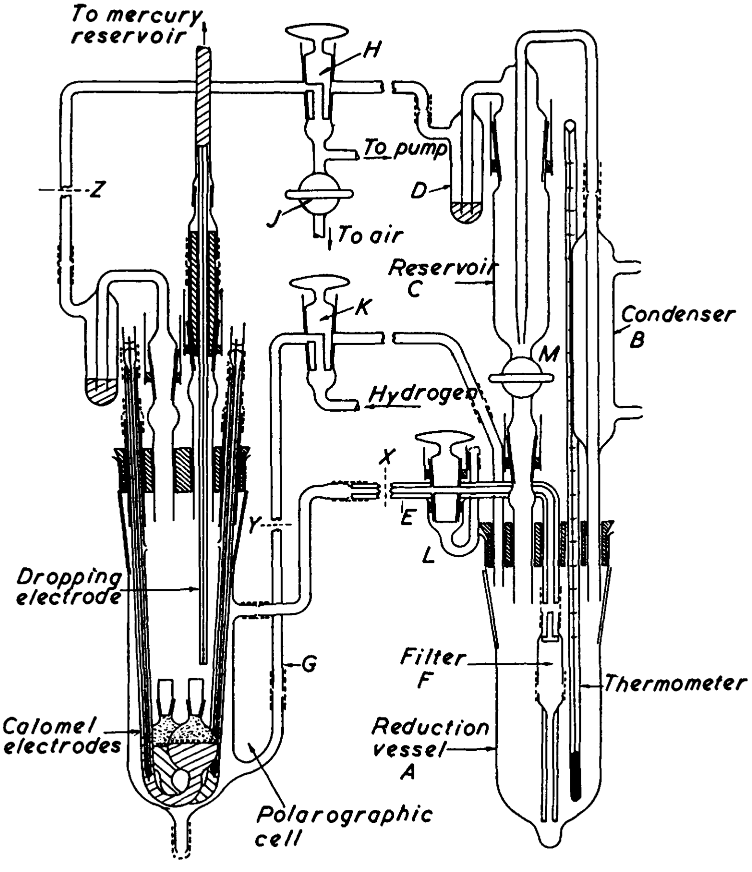
[15] Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948.

also necessitated reversing the polarity of the auxiliary and built-in standardising potentiometers. To facilitate this polarity reversal an 8-pole 2-way switch was used, permitting ready adjustment of the instrument for either oxidative or reductive polarography.

The ratio of successive current sensitivities provided by the polarograph, generally 2, was found to be too great for optimum use of the rather small chart width. The recorder galvanometer was therefore shunted to permit the sensitivity to be changed by factors of $\frac{3}{4}$ or $\frac{2}{3}$ as required.

Polarography and reduction were carried out in separate vessels, shown in Fig. 2, since heating was necessary during reduction. Pyrex glass was used throughout, except for the tubes carrying the external connections to the calomel electrodes, which were of soda glass into which platinum wire contacts were sealed. Flexible connections between glass tubes (broken lines in Fig. 2) were of poly(vinyl chloride) tubing. Water-jacketed condenser *B* condensed any ethanol vaporised during reduction of the dye in vessel *A*. Mercury-bubbler *D* isolated vessel *A* from the air. Reservoir *C* contained liquids (*e.g.*, acid buffer components) whose presence might interfere with the catalytic reduction of the dye in *A*; such liquids were added to the *leuco*-solution, after reduction, *via* tap *M*. Filter *F*, packed with glass wool, prevented catalyst from being carried over with *leuco*-solution during its transfer from *A* through tap *L* to the polarographic cell. Taps *H*, *K*, *L* and all ground-glass joints, other than those of which vessel *A* and the polarographic cell were constructed, were fitted with water seals.

FIG. 2.



The polarographic cell assembly was similar to that of Kaye and Stonehill; [8a] this type was considered more convenient than the usual H-type cell for evacuation, rigorous exclusion of air, and cleaning. The cathode was a dip-type saturated calomel electrode. A second similar electrode, which carried no current, permitted determination of the dropping-mercury electrode potential without errors due to ohmic potential drop. The calomel electrode vessels had a small hole in the main stem, above the liquid level, to permit equalisation of internal and external pressures during removal of air from the cell by evacuation, and also to permit thorough degassing of the electrode contents by evacuation after filling, thus preventing the formation of a high-resistance layer of gas bubbles underneath the small glass stopper. The electrodes, after being filled and degassed, were kept for 24 hr. before use. After each experiment they were washed externally with distilled water and, after their stoppers had been loosened, were immersed in distilled water until next required. Their potentials were periodically checked against each other and against a third electrode, and when, infrequently, they differed by 2 mv or more, the electrodes were refilled. When the polarographic cell resistance, calculated from the ohmic potential drop, rose significantly above the usual 5000 ohms, the glass stoppers of the electrodes were thoroughly flushed with the potassium chloride solution, which was replenished if necessary.

The polarographic cell was immersed in a well-stirred thermostatic water-bath, kept at 25° ± 0·02° by means of a metal 250-w immersion heater (to avoid photolytic effects of light bulbs), mercury–toluene thermoregulator, and electronic relay. The dye-reduction vessel was heated by immersion in a small water-bath (a 250 ml. glass crystallising dish) on an electric hot-plate controlled by a Simmerstat and three-heat switch. This bath was fitted with a cold water inlet and an overflow, to permit rapid cooling of the *leuco*-solution before transfer to the polarographic cell.

Reduction of Dyes.—Preliminary work on the reduction of Caledon Gold Orange G and Caledon Orange 2RTS with alkaline sodium dithionite showed that excess of dithionite was required for complete reduction, that the *leuco*-dyes gave polarographic oxidation waves at about $-0{\cdot}7$ v (against the saturated calomel electrode), and that, in agreement with earlier work,[9a] alkaline dithionite alone gave anodic waves in the same potential region. It was thus necessary to remove excess of dithionite to avoid interference with the dye waves. Attempts to do so by adding measured amounts of formaldehyde solution or by bubbling in known volumes of air were unsuccessful; formaldehyde addition caused a new wave to appear at about $-0{\cdot}4$ v; addition of air was difficult to control and probably caused some oxidation of *leuco*-dye. Further work was thus restricted to catalytic dye reduction. Preliminary tests with Raney nickel and Caledon Gold Orange G (one of the most difficult dyes to reduce) showed that a high reduction temperature is desirable, that reduction takes at least 30 min. for low dye concentrations and longer for higher concentrations, that it is facilitated by increasing the pH and by addition of ethanol, at least 8% of the latter being necessary, and that the catalyst is more effective if added before than after displacement of air from the system by hydrogen.

Freshly prepared nickel catalyst caused over-reduction of some dyes. Thus Caledon Orange 2RTS gave a solution which changed during reduction from the purple colour obtained by dithionite reduction to a dichroic orange; this, unlike the normal purple *leuco*-solution, became colourless on reoxidation with hydrogen peroxide and would not then give a coloured solution on reduction by dithionite. Although the over-active catalyst could be sufficiently deactivated by bubbling air through it for some minutes, the necessary re-evaluation of the deactivated catalyst was tedious. In such cases, therefore, a platinised or, better, a palladised asbestos catalyst proved suitable. However, some samples of these catalysts caused dehalogenation of some dyes: as no simple deactivation process was available for these catalysts, nickel catalysts were used for reducing these dyes. Each batch of nickel catalyst was tested for over-activity by reducing the halogenated dye Caledon Orange 2RTS with a sample for 1½ hr. at 70° and examining the solution polarographically for any shift of half-wave potential. No indication of partial dehalogenation was ever observed; a given batch of catalyst gave, according to its activity, a solution which yielded polarograms characteristic either of the undehalogenated dye or of its completely dehalogenated analogue, but never of both together.

Procedure.—A high ethanol concentration in the *leuco*-solution minimises adsorption effects on polarograms,[8] but causes precipitation of buffer salts; a compromise concentration of 48% ethanol was thus adopted. By postponing the addition of water or aqueous solution of acid buffer components until after reduction, the latter was facilitated by the availability of higher ethanol concentrations and higher pH.

A measured volume of well-shaken dye suspension was placed in reduction vessel *A* (Fig. 2), together with suitable quantities of ethanol, sodium hydroxide solution, catalyst, and water.

The required quantity of water or aqueous solution of acidic buffer component was placed in reservoir *C* together with a little catalyst, and the apparatus assembled. The reduction apparatus and the polarographic cell were isolated from each other by means of taps *H*, *K*, and *L*, and separately evacuated. Hydrogen was then passed in through the cell and thence through tap *L* into the reduction vessel until these were at atmospheric pressure, as indicated by a manometer in the vacuum-pump line. After a second evacuation and flushing with hydrogen, mercury-bubbler *D* was connected to the air by taps *H* and *J*, and hydrogen was slowly bubbled *via* filter *F* through the contents of the reduction vessel until dye reduction was complete (1—1½ hr.). Reduction temperatures were 45—50° for anthanthrone and Cibanone Golden Yellow GK, 50—55° for Cibanone Golden Yellow RK, 55—60° for Algol Yellow WG, Caledon Red X5BS, Cibanone Brilliant Orange GK, and Caledon Brilliant Orange 4RN, 60—65° for Caledon Red 5G, Caledon Brilliant Orange 6R, Caledon Orange 2RTS, and Caledon Blue RC, and 70—75° for Caledon Gold Orange G. The contents of reservoir *C* were then slowly added to the reduction vessel, which was cooled by filling the heating-bath with cold water. Tap *M* was closed, and tap *H* turned to connect the bubbler outlet from the cell to the air. Hydrogen was then passed through tap *K* directly into the reduction vessel, thus forcing the *leuco*-solution into the cell through filter *F*.

A preliminary polarogram was recorded with the 0·5 v/min. scanning speed and extended voltage sweep (−0·5 to −3·0 v), in order to determine the requisite voltage range and permit the adjustment of galvanometer zero, sensitivity, and counter-current. The cell was then disconnected, the voltage across the polarograph potentiometer reduced to 0·7 v, and the necessary biassing voltage applied with the auxiliary potential divider. The cell was then re-connected, any necessary zero-current adjustments made, and a polarogram recorded at the reduced voltage-scanning rate. At intervals of 0·1 v in the applied potential, the potential of the dropping-mercury electrode was measured to within 1 mv against the reference calomel electrode. From the linear graph of cell current against correction to the applied potential for ohmic drop across the cell, the correction for any given applied potential could be determined.

Polarograms were determined at mercury column heights, h, of 70, 58, 46, and 35 cm., and the slope of the graph of log i (i = wave-height) against log h was determined for each wave. Theoretically slopes of 0·5, 1·0, and 0—0·5 denote respectively diffusion, adsorption, and kinetic waves. In practice, slopes between 0·35 and 0·65 were assumed to correspond to diffusion waves, and higher and lower values to adsorption and kinetic waves respectively.

Since the *leuco*-solutions of some halogenated dyes underwent dehalogenation and oxidation on exposure to visible light, the reduction apparatus and polarographic cell were housed in a small light-tight cabinet.

For investigating the effect of irradiation on the polarograms, the micro-polarographic cell described elsewhere[16] was used. This permitted maximum irradiation of the dropping-mercury electrode surface region, in which the redox system is located in polarography, since a minimum thickness of *leuco*-solution was interposed between it and the radiation source. *leuco*-Solutions in 48% ethanol containing 0·1N-sodium hydroxide, prepared by hydrogen–nickel reduction, were transferred to the cell by the normal technique,[16] the whole operation being in the dark. The maximum possible volume of solution was retained in the cell to minimise concentration decrease due to electrolysis during polarography. Polarograms were recorded first in the dark, and then at 15 min. intervals during irradiation of the dropping-electrode surface region with a 300-w projection lamp giving a condensed beam 1½ in. in diameter, or with *X*-rays from a General Electric Model D portable *X*-ray generator. No corrections were made for ohmic potential drop, since only comparative results were required. The experiments with visible light were repeated with solutions to which 1 ml. of a 50% ethanolic solution of a mixture of potential mediators was added after reduction but before transfer to the cell. The mediator solution was 0·001M with respect to each of Methylene Blue, potassium indigotetrasulphonate, potassium indigodisulphonate, 1-aminoanthraquinone-8-sulphonic acid, sodium anthraquinone-2-sulphonate, 1-amino-4-bromoanthraquinone-2-sulphonic acid, 3-amino-anthraquinone-2-sulphonic acid, and 1 : 2-dihydroxyanthraquinone.

RESULTS

Because of the difficulty in preparing homogeneous dye suspensions and achieving complete reduction, the frequent multiplicity and poor definition of the waves, and the small recorder

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[16] Cooper and Stonehill, *J.*, 1958, 3362.

chart-width, the accuracy of the recorded data is limited in some cases to about 10% in wave-heights and 10 mv in half-wave potentials. The pH range employed was limited by precipitation of acid *leuco*-dye at lower pH values. The detailed polarographic results are given in Table 1, where A to E refer to the successive waves in order of increasingly negative $E_{\frac{1}{2}}$ given by a particular dye.

Algol Yellow WG gave two diffusion waves, A (partly kinetic) and B, with wave-height ratio A/B tending to about 1·15 at higher concentrations, independent of pH.

Caledon Red 5G gave, when reduced with a partially deactivated nickel catalyst, a cathodic wave at about $-0{\cdot}9$ v, in addition to two anodic waves. Since the cathodic wave suggested incomplete reduction, fresh fully active nickel catalyst was used in subsequent experiments. This resulted in three anodic diffusion waves, A, B, and C, with the same total height as the former cathodic plus two anodic waves. The height of C is independent of pH, while the height ratio B/A varies considerably with pH.

Caledon Red X5BS, like the preceding dye, required fresh nickel catalyst for complete reduction, and gave three diffusion waves, an additional small adsorption wave appearing at pH 12·88.

Anthanthrone, although not strictly a dye because of its low affinity for cellulose, was of interest as the parent compound of Cibanone Brilliant Orange GK and Caledon Brilliant Orange 6R. Two diffusion waves, A and B, were observed at all pH values; B is complicated by a small maximum no suppressed by 0·1% of gelatin, methylcellulose, or Methyl Red. The wave-height ratio A/B (the maximum being ignored) rises as pH falls.

Cibanone Brilliant Orange GK gave two diffusion waves, A and C; the latter had an associated adsorption after-wave D at pH 12·88, and an adsorption fore-wave B at lower pH. At any given pH, the wave-height ratio of C plus B or D to A varies with rise of concentration, tending to a limit of ~1.

Caledon Brilliant Orange 6R gave two diffusion waves, B, with an adsorption fore-wave A, and D, with an adsorption after-wave E at pH 12·88 and an adsorption fore-wave C at lower pH. The ratio of the heights of the diffusion waves, each together with its adsorption wave, varies with rise of concentration, tending to a limit of ~1.

Caledon Gold Orange G was difficult to reduce, requiring freshly prepared nickel catalyst at 70—80°. At all pH values a polarographic maximum was observed, not removable by adding various suppressors, although 0·01% of gelatin improved the wave form and was thus added throughout. A single diffusion wave C was observed, preceded at pH 12·88 and 12·12 by an adsorption wave B; at lower pH the latter split into two ill-defined steps A and B, similar to those reported for acridine.[8a]

Both Caledon Orange 2RTS and Caledon Brilliant Orange 4RN gave two diffusion waves, B and D. Each was associated with an adsorption fore-wave, A and C respectively, the latter occurring at pH 12·88 only. The wave-height ratio (A + B)/C + D) decreases with rise of concentration at constant pH, or with rise of pH at constant concentration.

Cibanone Golden Yellow GK gave a single diffusion wave with a maximum unaffected by 0·1% of gelatin, methylcellulose, or Methyl Red. At pH 12·88 the maximum was only slight, being indicated mainly by erratic galvanometer oscillations, but at lower pH it occurred as a broad hump. At pH 12·88 the polarograms were unsymmetrical, being drawn out at the more negative potentials, especially at lower concentrations. In Table 1, both maximum and minimum values of wave-heights are quoted.

Cibanone Golden Yellow RK gave at pH 12·88 two diffusion waves, B and C. As pH was decreased, the relative height of B fell until at pH 11·56 or below only C remained. An adsorption after-wave D occurred at pH 12·88, and an adsorption fore-wave A at lower pH.

Caledon Blue RC, the only halogenated dye examined which did not become dehalogenated when irradiated or electrolysed in *leuco*-solution, was not investigated at pH below 12·12 because of precipitation of the *leuco*-acid. It gave a single diffusion wave B, preceded at pH 12·12 only by an adsorption wave A.

In the study of the effect of irradiation on the polarograms of *leuco*-dyes, use was made of Caledon Gold Orange G, Cibanone Golden Yellow GK, Caledon Red 5G, and Caledon Blue RC. The first three are highly active, the last inactive, in tendering.[17,18] Apart from the last, they

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[17] Landolt, *J. Soc. Dyers and Colourists*, 1949, **65**, 659.

[18] Fox, *ibid.*, p. 508.

TABLE 1. *Half-wave potentials* vs *saturated calomel electrode and wave-heights.*

pH	c	$-E_{\frac{1}{2}}$ (mv)					i (μA)				
	(mM)	A	B	C	D	E	A	B	C	D	E
Algol Yellow WG; m = 3·207 mg./sec., t = 2·61 sec.; A kinetic-diffusion; B diffusion											
12·88	0·29	626	785				0·76	0·78			
,,	0·67	647	787				2·10	1·50			
,,	1·15	676	789				3·45	2·70			
12·12	0·48	626	779				1·29	1·17			
,,	0·96	669	769				2·51	2·34			
11·56	0·48	635	735				1·38	1·20			
,,	1·05	659	739				3·06	2·46			
11·15	0·48	630	732				1·20	1·15			
,,	0·96	651	737				2·76	2·28			
Caledon Red 5G; m = 3·310 mg./sec., t = 2·53 sec.; A, B, C diffusion											
12·88	0·70	402	535	731			1·28	0·24	1·24		
,,	1·40	409	532	728			1·95	0·68	2·62		
12·12	0·70	348	482	733			0·30	0·72	1·44		
,,	1·40	335	473	730			0·97	1·80	2·70		
11·56	0·70	327	458	697			0·51	0·60	1·29		
,,	1·40	307	448	690			1·26	1·62	2·16		
11·15	0·70	320	460	726			0·56	0·68	1·48		
,,	1·40	310	453	705			1·27	1·60	2·53		
Caledon Red X5BS; m = 3·286 mg./sec., t = 2·55 sec.; A, B, C diffusion; D adsorption											
12·88	0·55	513	645	761	892		0·27	0·56	1·01	0·27	
,,	1·22	519	637	770	879		0·53	1·23	2·19	0·58	
12·12	0·55	498	652	758			0·72	0·56	0·80		
,,	1·22	471	661	760			1·12	1·44	1·71		
11·56	0·55	458	663	769			0·56	0·56	0·83		
,,	1·11	449	648	764			0·75	1·33	1·82		
11·15	0·55	461	661	762			0·40	0·56	0·85		
,,	1·00	470	656	769			0·72	1·24	1·56		
Anthanthrone; m = 3·139 mg./sec., t = 2·67 sec.; A, B diffusion											
12·88	0·24	598	707				0·72	0·60			
,,	0·59	596	704				1·76	1·16			
,,	0·99	602	708				3·12	2·10			
12·12	0·48	605	705				1·72	1·00			
11·56	0·48	604	688				1·76	0·80			
11·15	0·24	599	688				0·80	0·33			
,,	0·48	603	696				1·80	0·60			
,,	0·95	600	687				3·60	1·47			
Cibanone Brill. Orange GK; m = 3·170 mg./sec., t = 2·64 sec.; A, C diffusion; B, D adsorption											
12·88	0·21	500		667			0·14		0·23		
,,	0·53	506		664	685		0·51		0·36	0·28	
,,	1·07	506		668	691		1·04		0·72	0·51	
,,	1·60	508		670	707		1·80		1·55	0·55	
,,	2·13	506		674	706		2·44		2·00	0·50	
,,	2·67	505		671	711		3·18		2·81	0·55	
12·12	0·53	548	610	647			0·71	0·30	0·35		
,,	1·21	551	618	652			1·52	0·36	1·04		
11·56	0·53	558	614				0·75	0·44			
,,	1·33	567	608	642			1·68	0·68	0·92		
11·15	0·40	553	614				0·71	0·41			
,,	1·21	565	612	636			1·52	0·64	0·74		
Caledon Brill. Orange 6R; m = 3·139 mg./sec., t = 2·67 sec.; B, D diffusion; A, C, E adsorption											
12·88	0·67	497	530		670	718	0·24	0·93		0·72	0·57
,,	1·35	504	531		676	726	0·30	1·98		1·92	0·60
12·12	0·40	488	530	610	647		0·06	0·58	0·30	0·35	
,,	1·48	539		655			2·40		2·56		
11·56	0·67	465	559	608	649		0·19	0·96	0·48	0·56	
,,	1·21	450	559	603	651		0·27	1·87	0·43	1·63	
11·15	0·27	470	553	612			0·21	0·34	0·32		
	1·35	480	563	602	648		0·27	2·08	0·48	1·68	

TABLE 1. (*Continued.*)

pH	c (mM)	$-E_{\frac{1}{2}}$ (mv)					i (μA)				
		A	B	C	D	E	A	B	C	D	E
Caledon Gold Orange G; m = 3·103 mg./sec., t = 2·70 sec.; C diffusion; A, B adsorption											
12·88	0·49		731	785				0·42	0·92		
,,	0·82		773					2·34			
12·12	0·33		712	756				0·18	0·72		
,,	0·41	—	706	753				0·17	0·97		
,,	0·82		704	762				0·15	2·28		
11·56	0·16	674	717				0·17	0·37			
,,	0·33	636	698	735			0·12	0·41	0·37		
,,	0·49	653	707	744			0·12	0·46	0·84		
,,	0·82	696		746			0·60		1·68		
11·15	0·41	664	733	754			0·20	0·45	0·48		
Caledon Orange 2RTS; m = 3·139 mg./sec., t = 2·67 sec.; B, D diffusion; A, C adsorption											
12·88	0·19	559	611	641	690		0·09	0·04	0·09	0·05	
,,	0·28	559	602	642	699		0·16	0·07	0·13	0·15	
,,	0·37	549	610	659	702		0·19	0·16	0·13	0·27	
,,	0·47	555	602	689			0·22	0·30	0·53		
,,	0·93	539	600	692			0·16	0·68	0·96		
,,	1·21	535	600	705			0·15	1·02	1·41		
,,	1·86	606		708			1·81		2·29		
12·12	0·58	524	633		700		0·22	0·88		0·46	
,,	1·16	530	643		710		0·33	1·47		0·84	
11·56	0·81	492	635		705		0·18	1·02		0·60	
,,	1·16	494	630		700		0·27	1·41		0·90	
11·15	0·70	496	631		704		0·18	0·90		0·36	
,,	0·93	499	634		714		0·21	1·46		0·45	
,,	1·39	494	638		719		0·24	1·76		0·68	
Caledon Brill. Orange 4RN; m = 3·139 mg./sec., t = 2·67 sec.; B, D diffusion; A, C adsorption											
12·88	0·22	518	547	618	682		0·09	0·06	0·08	0·21	
,,	0·36	513	563	609	680		0·10	0·12	0·07	0·51	
,,	0·49	518	560	605	687		0·11	0·15	0·06	0·67	
,,	0·90	519	565		692		0·10	0·44		1·22	
,,	1·17	492	560		684		0·12	0·54		1·71	
12·12	0·36	488	582		693		0·12	0·32		0·24	
,,	0·72	500	577		696		0·13	0·68		0·56	
,,	1·26	492	590		693		0·15	1·26		1·20	
11·56	0·36	452	580		691		0·10	0·34		0·30	
11·15	0·36	447	591		686		0·08	0·31		0·22	
,,	0·72	454	586		692		0·11	0·67		0·51	
Cibanone Golden Yellow GK; m = 3·139 mg./sec., t = 2·67 sec.; A diffusion											
12·88	0·19	673					0·69				
,,	0·47	663					1·66				
,,	1·32	668					4·70				
12·12	0·47	672					1·40,[a] 1·56[b]				
11·15	0·47	658					1·38,[a] 1·54[b]				
,,	0·94	664					2·86,[a] 3·27[b]				
Cibanone Golden Yellow RK; m = 3·139 mg./sec., t = 2·67 sec,; B, C diffusion; A, D adsorption											
12·88	0·31		630	693				0·44	0·37		
,,	0·61		621	665	719			0·82	0·46	0·36	
,,	1·02		623	669	718			1·52	0·88	0·40	
,,	1·53		620	674	726			2·13	1·55	0·37	
,,	1·94		619	683	738			2·80	2·40	0·34	
,,	2·35		612	678	738			3·45	2·84	0·37	
12·12	0·64	502	618	654			0·06	0·52	1·30		
,,	1·28	518	619	666			0·05	1·12	2·61		
11·56	1·28	524		656			0·20		3·12		
11·15	0·38	534		648			0·15		0·83		
,,	1·28	517		656			0·16		3·48		
Caledon Blue RC; m = 3·192 mg./sec., t = 2·70 sec.; A adsorption; B diffusion											
12·88	0·50		693					1·11			
,,	0·75		686					1·64			
12·12	0·50	574	677				0·17	1·01			
,,	1·25	564	686				0·12	2·72			

[a] Minimum value; [b] maximum value.

are unhalogenated and, unlike the other halogenated dyes in Table 1, do not undergo photo-oxidation in *leuco*-solution. (It is indeed surprising that Waly *et al.*[5] did not mention this photo-reaction which must have occurred during irradiation of various halogenated *leuco*-dyes they investigated.) Two concentrations were used for each dye, *viz.*, the highest which permitted observation of the dropping electrode, and the lowest which gave well-defined, reproducible waves. No change was observed in the polarograms of any of four dyes after irradiation with visible light for 1 hr., or for the first two dyes after exposure to X-rays for $\frac{1}{2}$ hr. Similar negative results were obtained on exposing all four *leuco*-dyes to visible light in the presence of the mixed potential mediator, which was of the same composition and used with similar concentrations of dye and mediator as in the work of Waly *et al.*[5] The small relative amount of mediator used was found to have a negligible effect on the dye polarograms in the dark.

DISCUSSION

In Table 2 are listed, for all the dyes examined, the values of the overall diffusion current constant I ($= i_{\text{total}}/cm^{2/3}t^{1/6}$), the number of diffusion waves, and the electron-loss per molecule (n) as obtained coulometrically.[16] In all cases I is independent of both c and pH, within experimental error. This argues against dye aggregation, which was suggested by Peters and Sumner[19] as a possible cause of deviations from a thermodynamic theory of adsorption on cotton of *leuco*-dyes at lower concentrations than those concerned here.

TABLE 2. *Diffusion current constants and coulometric electron losses.*

Dye	No. of main waves	I (overall)	n (electrons per mol.)
Algol Yellow WG	2	2·05	2
Caledon Red 5G	3	1·45	2
Caledon Red X5BS	3	1·39	2
Anthanthrone	2	2·09	2
Cibanone Brilliant Orange GK	2	0·95	1
Caledon Brilliant Orange 6R	2	1·33	1
Cibanone Golden Yellow GK	1	1·40	2
Cibanone Golden Yellow RK	2	1·09	1
Caledon Gold Orange G	1	1·14	2
Caledon Orange 2RTS	2	0·85	1
Caledon Brilliant Orange 4RN	2	0·78	1
Caledon Blue RC	1	0·90	2
Cibanone Blue RSN[16]	1	0·93	2

For the dyes giving a single main wave, n is 2, suggesting a one-stage electro-oxidation of quinol to quinone represented by: $R(O^-)_2 - 2e \longrightarrow RO_2$, the quinol being fully ionised since the $E_{\frac{1}{2}}$ values for the main waves are practically independent of pH over the range studied.

For the dyes giving two main waves, the value of n is 2, except for those dyes which in *leuco*-solution undergo dehalogenation and oxidation in light or upon electrolysis;[16,20] for the latter, the coulometric n-value is 1. However, a comparison of I-values suggests that actually n is 2 for all these dyes, if due allowance is made for the effect of halogenation in increasing molecular size and mass, thus decreasing the diffusion coefficient and I. The I-values for unbrominated Caledon Gold Orange G (1·14) and its di- and tri-bromo-derivatives Caledon Orange 2RTS (0·85) and Caledon Brilliant Orange 4RN (0·78) illustrate this point. The only anomaly is this respect is that I for the bromo-dye Caledon Brilliant Orange 6R is greater than the value for the chloro-analogue, Cibanone Brilliant Orange GK. A possible reason is the greater degree of hydration of the molecule containing the more electronegative chlorine atoms.

The dyes in the two-wave class differ amongst themselves as regards the relative total heights (*i.e.*, including related adsorption waves) of the two main waves and their variation with pH. For Algol Yellow WG, Cibanone Brilliant Orange GK, and Caledon Brilliant Orange 6R, the two wave-heights are approximately equal at all pH values employed. Here the two steps may represent successive one-electron oxidations *via* the semiquinone.

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[19] Peters and Sumner, *J. Soc. Dyers and Colourists*, 1957, **73**, 12.

[20] Cooper and Stonehill, following paper.

For anthanthrone, Caledon Orange 2RTS, and Caledon Brilliant Orange 4RN, the total height of the wave with more positive $E_{\frac{1}{2}}$ is greater than that of the other wave, except at pH 12·88 for the last two halogenated dyes, and increases relatively as pH falls. The sum of the two total wave-heights per unit *c*, however, is independent of pH. Unequal wave-heights could arise from distortion due to polarographic maxima, difference in diffusion coefficients of quinol and semiquinone due to aggregation or complexing with buffer, or limited solubility of quinol or semiquinone. For any of these, pH variation would affect not only the wave-height ratio but also the overall wave-height, contrary to observation.

Pyruvic acid gives on polarographic reduction two waves with pH-dependent height ratio but constant aggregate height.[21] This was explained [22] by ascribing the waves to two different species, the ionised and the un-ionised acid, with different $E_{\frac{1}{2}}$ values, and with relative amounts controlled by a pH-dependent equilibrium whose rate of attainment is slow compared with the electrochemical reduction rate, so that the system is thermodynamically reversible but polarographically irreversible. A similar explanation might apply to the present results, based on the effect of pH variation on either the degree of ionisation of the quinol or the extent of quinol–oxanthrol tautomerisation. The ionisation equilibration is almost certainly too fast to give rise to extra waves, judging from the fact that many anthraquinols under conditions in which they were incompletely ionised gave only a single polarographic wave for a given redox step.[9a] The alternative assumption of a relatively slow quinol–oxanthranol tautomerisation,

$$\mathrm{R(O^-)_2} + 2\mathrm{H^+} \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} \mathrm{R(OH)_2} \overset{\text{Slow}}{\rightleftharpoons} \mathrm{O{:}RH{\cdot}OH}$$

has been confirmed for certain hydroxyanthraquinols.[9b] Such tautomerism is well known in anthraquinonoid *leuco*-dyes.[23] We may suppose that in polarographic oxidation the oxanthranol wave has a more positive $E_{\frac{1}{2}}$ than the quinol wave, because the quinol is present partly as negative ions; this is supported by a comparison of the $E_{\frac{1}{2}}$ values of the two waves with the $E_{\frac{1}{2}}$ value of a chemically similar molecule which gives only a single (quinol) oxidation wave, *e.g.*, Cibanone Gold Yellow RK compared with Cibanone Gold Yellow GK, or Caledon Orange 2RTS and Caledon Brilliant Orange 4RN with Caledon Gold Orange G. On this basis, the wave-height ratio of quinol to oxanthranol decreases with fall of pH for anthanthrone, Caledon Orange 2RTS, and Caledon Brilliant Orange 4RN, but increases for Cibanone Gold Yellow RK which at pH 11·56 and below gives no oxanthranol wave. The decrease is due to the shift of the tautomerisation equilibrium to the right as pH falls. The increase for the last-mentioned dye may be tentatively ascribed to the faster tautomerisation, which is presumably catalysed by hydrogen ions; when the tautomerisation rates exceed the electro-oxidation rate, the oxanthranol wave disappears. However, it must be mentioned that the rate of tautomerisation of 2-hydroxyanthraquinol is apparently independent of pH.[9b] If these two opposing effects of pH variation on the quinol–oxanthranol wave-height ratio are accepted, they could roughly balance over a limited pH range; this would provide an alternative explanation of the roughly pH-independent wave-height ratio, not quite equal to unity, found for Algol Yellow WG, Cibanone Brilliant Orange GK, and Caledon Brilliant Orange 6R. The partly kinetic nature of the Algol Yellow WG wave at more positive potentials, the parallelism between the $E_{\frac{1}{2}}$ values of both waves for the last two dyes, and for their unhalogenated analogue anthanthrone, and the potentiometric indication (Table 3) that the last dye forms no stable semiquinone, all accord with this view.

Three anodic diffusion waves of unequal heights are given by Caledon Red 5G and Caledon Red X5BS when reduced with an active catalyst, but only two anodic waves and a cathodic wave with a partially deactivated catalyst. The overall coulometric *n*-value is

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[21] Müller and Baumberger, *J. Amer. Chem. Soc.*, 1939, **61**, 590.

[22] Brdicka and Wiesner, *Coll. Czech. Chem. Comm.*, 1947, **12**, 138.

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

always 2. The cathodic wave occurs at a similar potential (about —0·9 v) to that of the cathodic wave obtained in one experiment with Caledon Red 5G in which catalyst was inadvertently omitted; nevertheless, it is unlikely to be the reduction wave of unreduced dye, since both of these dyes are appreciably soluble in aqueous ethanol and thus readily reduced even with less active catalyst in the cold, and also because the wave-height is approximately proportional to concentration. Now Coffey[23] reported that Caledon Red 5G readily formed an oxanthranol which is easily reduced to the anthrone, and easy reduction of other anthraquinone derivatives to anthrones by sodium dithionite has also been observed.[24] It is thus probable that, with the less active catalyst, the dye quinone is reduced to the quinol and its tautomeric oxanthranol, which account for the two anodic waves, as for the dyes giving only two waves, while the cathodic wave is due to polarographic reduction of oxanthranol to anthrone. With the more active catalyst, it is probable that all the oxanthranol is reduced to the oxanthrone and its tautomeric anthranol

$$\mathrm{O{:}RH{\cdot}OH} \xrightarrow{\text{Redn.}} \mathrm{O{:}RH_2} \rightleftharpoons \mathrm{HO{\cdot}R{\cdot}H}$$

as fast as it is formed by tautomerisation of the quinol; the *leuco*-solution thus contains quinol, anthrone, and anthranol, which give rise to three anodic oxidation waves. Their aggregate height is proportional to *c* and independent of pH, but at any given pH their relative heights vary somewhat, probably because of variable extents of oxanthranol formation followed by over-reduction to anthrone and anthranol. Comparison of $E_{\frac{1}{2}}$ values with those of the related benzamidoanthraquinone, Algol Yellow WG, indicates that the wave with the most negative $E_{\frac{1}{2}}$ is due to the quinol. That one of the three oxidisable species in the *leuco*-solution is an impurity is unlikely in view of the relatively large wave-heights observed; nor is it likely to be a hydrolysis product of the dye produced during reduction, since, although these benzamidoanthraquinones are reported to undergo hydrolysis under severe vatting conditions,[18] their appreciable solubility rendered high temperatures unnecessary during reduction.

Appleton and Geake[2b] determined potentiometrically the redox potentials, in 0·1N-sodium hydroxide, of three of the dyes concerned here. Although the solvent (50% aqueous pyridine) and temperature (50°) are different, comparison with the present results for the same alkalinity, as in Table 3, is of interest. The first two dyes, and probably also the third, give a single 2-electron polarographic wave for the oxidation of quinol to quinone, while potentiometrically the first two give two discrete one-electron redox steps, indicating the formation of a stable semiquinone; there appears to be no simple relation between polarographic $E_{\frac{1}{2}}$ values and potentiometric standard redox potentials. Since most, if not all, of the dyes in Table 1 give a single wave for the polarographic oxidation of the quinol, despite considerable variation in fading and tendering activity, it is clear that polarography is incapable of revealing whether such activity is related to semiquinone formation.

TABLE 3. *Comparison of potentiometric and polarographic results.*

Dye	Potentiometric standard redox potentials (mv) [a]	Polarographic half-wave potentials (mv) [b]
Caledon Gold Orange G	—564, —616	—780
Cibanone Golden Yellow GK	—490, —658	—668
Caledon Brilliant Orange 6R	—581	—530, —673

[a] In 0·1N-NaOH, 50% aqueous pyridine, 50° (ref. 2*b*). [b] In 0·1N-NaOH, 48% aqueous ethanol, 25°.

When the dyes examined are placed in order of increasing $E_{\frac{1}{2}}$ for the quinol oxidation step, it appears that, despite some variation in the order with change of pH, there is some correlation with light-fastness, which decreases as $E_{\frac{1}{2}}$ becomes more negative. No such correlation of $E_{\frac{1}{2}}$ with tendering activity is apparent.

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[24] Bradley and Maisey, *J.*, 1954, 274.