681. *Fading and Tendering Activity in Anthraquinonoid Vat Dyes.*
Part VI.* The Coulometry of the Polarographic Oxidation of leuco-
Dyes.

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The number of electrons per molecule involved in the polarographic
oxidation of *leuco*-solutions of 12 anthraquinonoid vat dyes and one related
quinone was determined micropolarographically. It is 2 for all the com-
pounds except those five which are halogenated and undergo photo-de-
halogenation–oxidation in *leuco*-solution; for these, the apparent number
of electrons is one. By conventional and differential absorption spectro-
scopy the products of the exhaustive polarographic oxidation of the di-
halogenated photo-active *leuco*-dyes are shown to contain about 25 moles %
of the analogous unhalogenated dye. Both this partial dehalogenation and
the low electron loss during electro-oxidation are accounted for by a tentative
reaction scheme in which a *leuco*-dye molecule adsorbed on the mercury-drop
anode is dehalogenated by the joint action of mercury and water, either
during or after electro-oxidation, yielding mercury halide and a hydroxyl
radical, which then oxidise another *leuco*-dye molecule.

IN order to interpret the oxidative polarograms of the *leuco*-dyes described in Part IV,[1]
a knowledge was required of the number (n) of electrons per molecule involved in the
oxidations. Logarithmic analysis was inapplicable since the polarographic waves are
irreversible. For the benzamidoanthraquinols, the insertion in the Ilković equation [2]
of a diffusion coefficient equal to the average value for some substituted anthraquinols,
estimated from Gill and Stonehill's polarographic data,[3] led to indeterminate n values.
Accordingly, Gilbert and Rideal's micropolarographic method [4] was used to provide
essentially coulometric n values under electrolysis conditions virtually identical with those
of macropolarography. In this method, a small volume (v litres; *ca.* 0·25 ml.) of solution,
of concentration c mole/l., is electrolysed at the dropping-mercury electrode at a potential
corresponding to a point on the diffusion–current plateau. The gradually decreasing
wave-height i is measured periodically, and, from the slope of the linear graph of log i
against t (duration of electrolysis in sec.), n is calculated by means of the equation

$$n = -i_0/2\cdot303\ cv\mathrm{F}\ (\mathrm{d}\log i/\mathrm{d}t)$$

where i_0 is the value of i for $t = 0$.

To investigate the extent of dehalogenation during the electrolysis of halogenated
leuco-dyes, the products of exhaustive electrolysis were examined by conventional and
differential absorption spectroscopy.

EXPERIMENTAL

Apparatus and Materials.—A micropolarographic cell was designed to permit about 10^{-7}
mole of *leuco*-dye, completely oxidisable by only 0·006 ml. of air, to be protected from atmo-
spheric oxidation for several hours. The cell (see Figure) was connected at X, Y, and Z to the
correspondingly lettered parts of the dye-reduction apparatus described previously.[1] The
broken lines represent connections or caps made of poly(vinyl chloride) tubing. The solution
undergoing electrolysis in tube A, in contact with the minimum volume of gas, floated on a
column of mercury kept at constant level, despite influx of mercury from the dropping electrode,
by overflow through tap E into vessel B. A U-tube, one end of which projected just above the

* Part V, preceding paper.
[1] Cooper and Stonehill, *J.*, 1958, 3341.
[2] Ilkovic, *Coll. Czech. Chem. Comm.*, 1934, **6**, 498.
[3] Gill and Stonehill, *J.*, 1952, 1845.
[4] Gilbert and Rideal, *Trans. Faraday Soc.*, 1951, **47**, 396.

mercury level in *A*, where it was closed with a small ground-glass stopper, was filled to the stopper with saturated aqueous potassium chloride solution. Into this dipped, in the other limb of the U-tube, an external cathode of silver wire coated anodically with silver chloride and welded to a platinum wire fused through the sealed end of the limb. Tap *E* was closed during removal of air from the apparatus by evacuation, thus preventing flow of mercury into *B* if a pressure difference existed between *A* and *B*. Tap *F*, normally kept closed, permitted equalis-ation of pressures in *A* and *C* when necessary. The volume of solution undergoing electrolysis was controlled by the level of the mercury overflow tube in *B* and that of the capillary jet terminating at the upper surface of the solution. Vessel *C* accommodated excess of *leuco*-solution and formed a trap preventing diffusion of any residual oxygen into *A*; it was provided with a mercury-filled bubbler gas outlet to *Z*. The lower end of *D*, containing *leuco*-solution, acted as a gas bubbler and oxygen trap. All of the smaller ground-glass joints were water-sealed against air-leakage. The previously boiled-out potassium chloride solution in the U-tube was thoroughly degassed by repeated evacuation in the assembled apparatus, thus
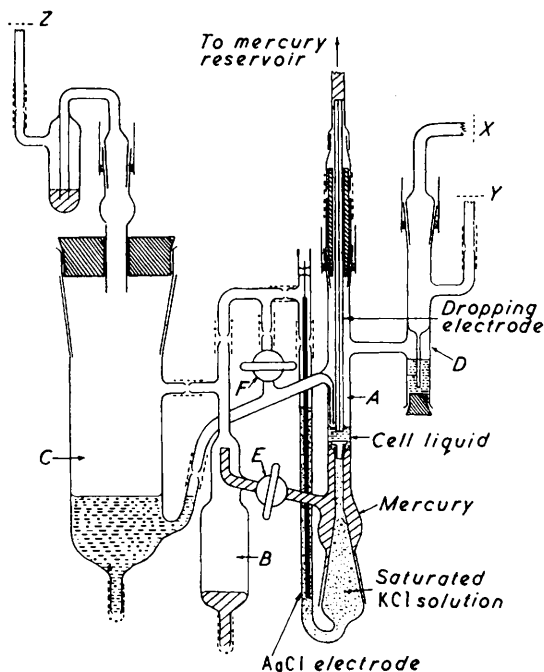
preventing the development of gas bubbles and a high electrical resistance at the glass stopper. After filling of the lower part of the apparatus with mercury, a similar degassing was required, to prevent an air-lock developing in tap *E*.

The polarograph, associated apparatus and materials used were as described in Part IV.[1]

Procedure.—Reduction of dye to give 25 ml. of *ca.* 10^{-3}M-*leuco*-solution in 48% v/v aqueous ethanol containing 0·1N-sodium hydroxide was performed as described previously for macro-polarography.[1] Before the reduction, the entire apparatus was evacuated and flushed with hydrogen three times to remove air; after reduction, the electrolysis cell alone was evacuated and flushed twice. With tap *E* closed, *leuco*-solution was forced by hydrogen pressure from the reduction vessel through the glass-wool filter and tube *X* into the cell, and followed by a little hydrogen through tube *Y* to ensure displacement of excess of solution into *C*. Tap *E* was then opened and tap *F* momentarily opened to equalise pressures in *A* and *C*. The glass-wool filter was well compacted, since incomplete removal of catalyst from the solution would lead to reduction of polarographically oxidised dye, with consequent high *n* values.

The solution in the cell was electrolysed at a potential corresponding to the diffusion–current plateau. At intervals, the complete polarographic wave was recorded to determine the wave-height. The recording took 2 min., during which the average current within one

drop-life fell from a maximum to zero, and was taken to be equivalent in effect to electrolysis for 1 min. at the maximum value.

The Gilbert–Rideal method for determining n involves the assumption that the wave-height falls only during electrolysis. For most *leuco*-solutions examined, however, the wave-height fell even when no current was passing, but less rapidly than during electrolysis. This is probably an oxidation effect. In some experiments the non-electrolytic fall occurred only when mercury flowed from the dropping electrode, and could be obviated temporarily by washing the mercury with dithionite solution to remove the oxidant (presumably a mercury oxide) responsible. Various well-known mercury-purification procedures led to only a brief improvement. In some other experiments the non-electrolytic decrease was rapid and practically independent of whether mercury was flowing; the presence of residual traces of some oxidant impurity cannot be excluded as an explanation here. A possible source of oxidant is air gradually evolved from the poly(vinyl chloride) tubing; this material is known to degas continuously under a vacuum.[5]

In general, the graphs of log i against t consisted of three linear sections, the first (pre-electrolysis period) being parallel to the third (post-electrolysis) and less steep than the second (electrolysis period). Hence the non-electrolytic decrease of i follows first-order kinetics, as does the electrolytic decrease. The difference between the slopes of the first and the second section thus gives the rate of change of log i due solely to electrolysis. This residual slope was inserted in the equation to determine n. Occasionally the pre-electrolysis graph exhibited initial curvature, generally associated with failure of the mercury drops from the electrode to coalesce, probably because of the presence of oxidant impurities in the cell. In such cases, no electrolysis was attempted until the graph became linear.

After periods of electrolysis and pre- and post-electrolysis long enough to permit accurate determination of the slopes of the three sections of the graph, the solution in A was removed with a capillary pipette and weighed. Its volume was calculated from its density, which was assumed to be the same for all the solutions electrolysed, and was determined for one of them with a hydrometer.

The direct determination of the true zero polarographic current line was not permitted by the characteristics of the Tinsley polarograph used. The zero line was at first assumed to coincide at any stage of the electrolysis with the bottom of the polarographic wave, which was taken to be wholly anodic. During the electrolysis of the benzamidoanthraquinols, however, the bottom as well as the top of the wave shifted towards lower current values. This, together with the high n values calculated on the assumption of a completely anodic wave, suggested that the oxidised dye was appreciably soluble in the ethanolic solvent (confirmed spectrophotometrically) and thus contributed a cathodic portion to the total wave-height. To correct for this, it was assumed that the freshly prepared *leuco*-solution was free from quinone, so that the first polarogram recorded was entirely anodic, the bottom of the wave coinciding with the zero-current line. The correction to the instrument zero thus obtained was applied unchanged to subsequent polarograms except when an alteration of the instrument sensitivity was necessary; in the latter eventuality, polarograms were recorded immediately before and after the alteration so that the zero-current correction for the new sensitivity could be determined.

Most of the *leuco*-solutions after electrolytic or pre-electrolytic oxidation tended to prevent coalescence of the mercury drops falling from the electrode, probably owing to strong adsorption of dye quinone on the drop surfaces. When severe, this effect led to a piling up of the discrete drops in the cell, without the normal overflow of mercury, until the cell became short-circuited and electrolysis was prohibited. When it was less severe, the drops coalesced after a few minutes or on tapping the cell; although with care electrolysis was then possible, the cell solution tended to become trapped between the mercury drops and carried below the mercury surface, thus decreasing the volume of solution electrolysed. Since the rate of electrolytic oxidation is proportional to *leuco*-dye concentration, drop-piling during electrolysis was minimised by keeping the concentration to the minimum consistent with the production of satisfactory polarograms; even so, with some dyes it was still necessary to tap the cell periodically during the earlier stages of electrolysis to induce coalescence. Pre-electrolytic oxidation by impurities was most evident after the apparatus had remained unused for some time, or had been cleaned and refilled with fresh mercury. Since in these circumstances oxidation of mercury was apparently responsible, the mercury surface was cleaned by filling

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[5] Gore, *J. Sci. Instr.*, 1957, **34**, 459.

the cell with warm alkaline dithionite and after some time rinsing with water. Any remaining pre-electrolysis piling was allowed to subside before measurements were started. Attempts to minimise drop-piling by adding various cationic, anionic, and non-ionic surface-active agents to the solution had little success.

Preparation of Electrolysis Products of Halogenated leuco-*Dyes for Spectroscopic Examination.*— To obtain the maximum quantity of each product under polarographic conditions, separate electrolyses were carried out in the micro-cell in which electrolysis started immediately after introduction of the *leuco*-solution and was continued until oxidation was almost complete. The solution was then exposed to air in the dark to complete oxidation without photo-dehalogenation, and the resulting suspension removed with a micro-pipette. The mercury in the cell was thoroughly washed with water injected beneath its surface, in order to recover the appreciable quantity of solid product carried below the mercury surface by drop-piling, which occurred with all the halogenated dyes. The combined washings and suspension removed from the cell were extracted with a minimum quantity of boiling chlorobenzene, and the extract was dried (CaO). The small volume of very dilute chlorobenzene solution thus obtained was placed on a layer of 5 ml. of mercury in a 4 cm. absorption cell, and its visible absorption spectrum determined with the Hilger Uvispek instrument, the aperture being used to limit the light beam so that it cleared the mercury. Both conventional (solvent in reference cell) and differential [6] spectra (solution of original dye, adjusted to the same concentration as in the test sample, in reference cell) were obtained.

RESULTS

A typical complete set of electrolysis results is given for Caledon Gold Orange G in Table 1, and the results for all the dyes examined are summarised in Table 2.

Algol Yellow WG gave initially n values of about 1.0. Spectrophotometric examination of the electrolysis product disclosed no evidence of decomposition. Thus the low n values were probably due to the presence of considerable impurity in the dye sample. With a specially synthesised and purified sample,[1] the expected value $n = 2$ was obtained.

TABLE 1. *Electrolysis of* leuco-*Caledon Gold Orange G.*

0.28 ml. of *leuco*-solution, initial concn. 0.855×10^{-3}M, electrolysed at -0.3 v $vs.$ S.C.E. Initial wave-height 2.60 μA.

$t/60$ (min.)	0	30 [a]	65	95	125	155	195	225	255 [b]
$10^6 i$ (A)	2·60	2·60	2·52	2·44	2·36	2·24	2·20	2·16	2·08
$t/60$ (min.)	285	315	345	375	420 [c]	455	485	515	
$10^6 i$ (A)	1·84	1·62	1·42	1·26	1·12	1·07	1·04	1·00	

[a] Hg flow started. [b] Electrolysis started. [c] Electrolysis ceased.

$$-\mathrm{d} \log i/\mathrm{d}t \text{ before electrolysis } 0.074 \times 10^{-4} \text{ sec.}^{-1}$$
$$\text{,, during ,, } 0.305 \text{ ,, ,,}$$
$$\text{,, after ,, } 0.082 \text{ ,, ,,}$$
$$\text{,, due to ,, } 0.231 \text{ ,, ,,}$$

$$n = 2.60 \times 10^{-6}/2.303 \times 0.855 \times 10^{-3} \times 0.28 \times 10^{-3} \times 96{,}500 \times 0.231 \times 10^{-4} = 2.12.$$

Cibanone Golden Yellow RK gave during one electrolysis a wave which, after initially decreasing in height, then increased several-fold rapidly; concurrently, mercury piling, normally severe with this dye, ceased completely, and the electrode drop-time increased considerably. In other runs the abnormally large wave-height appeared as soon as electrolysis started. The abnormalities disappeared when the vatting temperature was lowered from 65° to 45° for this dye, which the manufacturers recommend should be cold-vatted. The enhanced waves appear to be catalytic. Wiesner [7] obtained catalytic waves during the polarographic oxidation of quinol and other reduced substances in the presence of hydrogen and a palladium catalyst, owing to reduction by active hydrogen of the anodic oxidation product as it was formed at the electrode. In view of the lengthened drop-time and the use of a filter to remove catalyst, this explanation is unlikely here.

All the dyes examined possess two reducible nuclear carbonyl groups per molecule (for the indanthrones Cibanone Blue RSN and Caledon Blue RC, only two of the four keto-groups are

[6] Cooper and Stonehill, *J.*, 1958, preceding paper.
[7] Wiesner, *Z. Elektrochem.*, 1943, **49**, 164.

normally reduced). The coulometric value $n = 2$ obtained for many of the dyes (Table 2) is thus as expected. For those halogenated *leuco*-dyes which undergo photo-dehalogenation,[6] n is about 1, suggesting partial dehalogenation during electrolysis. The conventional and differential visible absorption maxima of the electrolysis products of four of the latter dyes are given in Table 3, along with comparative data for the original dyes and their unhalogenated

TABLE 2. *Summary of results of oxidative coulometry.*

| | | | -10^5 d log i/dt | | |
| | | | before | during | |
Dye	i_0/c	10^3v	electrolysis	electrolysis	n
Algol Yellow WG	4·65	0·45	0·67	2·90	2·08
		0·30	0·85	4·24	2·06
Caledon Red 5G	4·46	0·43	0·82	2·95	2·17
		0·47	0·27	2·22	2·19
Caledon Red X5BS	4·10	0·32	0·00	2·72	2·11
Anthanthrone	5·45	0·23	0·12	5·28	2·07
		0·36	0·49	4·03	1·93
Cibanone Brilliant Orange GK [a]	3·00	0·27	0·73	6·35	0·89
		0·26	2·23	8·00	0·90
		0·28	1·17	5·97	1·00
Caledon Brilliant Orange 6R [a]	3·89	0·34	0·03	5·54	0·94
		0·29	0·41	7·06	0·91
		0·30	0·44	5·98	1·05
Cibanone Golden Yellow GK	4·32	0·36	0·25	2·72	2·18
		0·29	0·91	3·98	2·18
Cibanone Golden Yellow RK [a]	3·01	0·32	0·28	4·71	0·96
		0·27	0·73	6·05	0·94
Caledon Gold Orange G	3·04	0·28	0·74	3·05	2·12
		0·26	0·56	3·54	1·77
		0·28	0·58	2·96	2·05
Caledon Orange 2RTS [a]	2·48	0·31	0·16	3·90	0·97
		0·26	0·00	4·50	0·95
Caledon Brilliant Orange 4RN [b]	1·96	0·46	2·29	4·31	0·95
		0·38	2·29	4·91	0·89
		0·30	3·79	6·83	0·96
Cibanone Blue RSN	3·74	0·26	0·56	3·77	2·01
		0·37	2·62	4·62	2·27
		0·33	3·00	5·61	1·96
Caledon Blue RC	3·62	0·41	2·18	4·26	1·91
		0·29	2·19	4·75	2·19

[a] Photoactive. [b] Photoactive; electrolysed for only $\frac{1}{2}$ hr. owing to mercury-piling.

TABLE 3. *Absorption maxima of leuco-dye electrolysis products.*

[Wavelengths of conventional (λ_c) and differential (λ_d) maxima are given in mμ, with optical densities (4 cm. cells) in parentheses. Differential maxima were obtained by placing in the reference cell a solution of the original dye, adjusted to the concentration at which it was present in the test sample; the absorption maxima of this reference solution are given under the last column heading.]

| | Electrolysis product | | Unhalogenated analogue | Original dye |
Dye	λ_c	λ_d	λ_c	λ_c
Cibanone Brilliant Orange GK	492 (0·89)	480 (0·21)	478	492 (0·80)
	463 (0·71)	450 (0·15)	450	465 (0·55)
Caledon Brilliant Orange 6R	490 (0·55)	480 (0·15)	478	492 (0·45)
	461 (0·48)	450 (0·09)	450	462 (0·39)
Caledon Orange 2RTS	487 (0·41)	473 (0·10)	474	488 (0·39)
	455 (0·23)	442 (0·06)	443	456 (0·20)
Cibanone Golden Yellow RK	471 (1·14)	466 (0·28)	466	473 (0·95)
	442 (0·83)	436 (0·18)	436	443 (0·70)

analogues.[6] The conventional maxima of the electrolysis products exhibit a slight hypsochromic shift of 1—2 mμ towards those of the unhalogenated analogues, but the results are inconclusive, since the concentrations and thus the absorbancies were low, leading to broad maxima with uncertain peak wavelengths. The differential absorption maxima, however, provide positive proof of partial dehalogenation. The optical densities of the differential

maxima are *ca.* $\frac{1}{3}$—$\frac{1}{4}$ of those of the corresponding maxima of the reference solutions of the original dyes. If similar molar extinction coefficients are assumed for the original dye and the unhalogenated analogue, this suggests that about 20—25% of dehalogenation has occurred. For *leuco*-Caledon Brilliant Orange 4RN the preparation for spectroscopic investigation of a sample of the exhaustive electrolysis product was impossible, owing to severe mercury-piling after about $\frac{1}{2}$ hour's electrolysis.
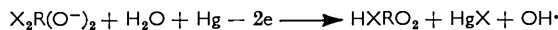
DISCUSSION

The dehalogenation accompanying electrolysis of the photo-active *leuco*-dyes must occur either during or after the electrolysis, which, under the conditions employed, yields exclusively dye quinones at the dropping-mercury electrode surface. These dyes are all strongly adsorbed on the electrode, as shown by the adsorption waves obtained during macro-polarography,[1] as well as by the particularly pronounced mercury-piling during micro-polarography. The diffusion current constants[1] indicate that the electrode reaction corresponds to $n = 2$. The apparent value $n = 1$ thus requires that half of the *leuco*-oxidation is electrochemical, the other half being chemical and occurring well away from the electrode surface in order not to affect the diffusion of fresh *leuco*-dye to the electrode. The 25% dehalogenation observed necessitates that water be decomposed to provide hydrogen which replaces halogen. The overall process may thus be written:
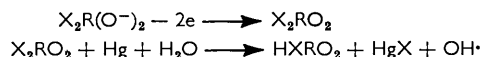
$$2X_2R(O^-)_2 + H_2O - 2e \longrightarrow 1\tfrac{1}{2}X_2RO_2 + \tfrac{1}{2}H_2RO_2 + X^- + OH^-$$
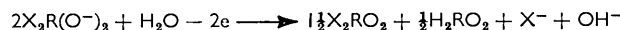
with a corresponding equation for the tautomeric oxanthranol:

$$2O\colon RX_2H\cdot OH + 3OH^- - 2e \longrightarrow 1\tfrac{1}{2}X_2RO_2 + \tfrac{1}{2}H_2RO_2 + X^- + 3H_2O$$

The following mechanism is tentatively suggested. The mercury abstracts a halogen atom from a dye molecule adsorbed on the electrode, forming mercury halide, whilst a water molecule in the solvent sheath or hydration shell releases a hydrogen atom to replace the halogen, producing a hydroxyl radical. This process may occur either during the bivalent electrolytic oxidation of adsorbed quinol (or oxanthranol):

$$X_2R(O^-)_2 + H_2O + Hg - 2e \longrightarrow HXRO_2 + HgX + OH\cdot$$

or after the electrolytic oxidation:

$$X_2R(O^-)_2 - 2e \longrightarrow X_2RO_2$$
$$X_2RO_2 + Hg + H_2O \longrightarrow HXRO_2 + HgX + OH\cdot$$

The mercury-piling effect might be due at least in part to the HgX film on the drop surface. The products thus formed diffuse away from the electrode or are carried away by the falling mercury drop. The hydroxyl radical and the mercury halide are capable of, and stoicheiometrically sufficient for, oxidation of a further molecule of dye quinol (or oxanthranol):

$$X_2R(O^-)_2 + OH\cdot + HgX \longrightarrow X_2RO_2 + OH^- + Hg + X^-$$
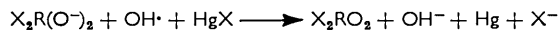
As before,[6] the monohalogenated dye is presumed to disproportionate:
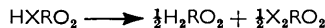
$$HXRO_2 \longrightarrow \tfrac{1}{2}H_2RO_2 + \tfrac{1}{2}X_2RO_2$$

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