SEMIQUINONE FORMATION BY ANTHRAQUINONE AND SOME SIMPLE DERIVATIVES.

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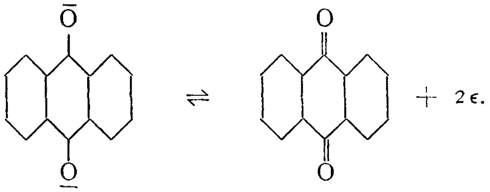
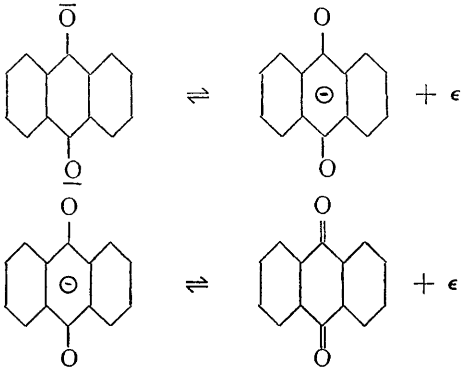
In the process of dyeing with an anthraquinonoid vat dye, the highly insoluble dye is first brought into solution by reduction in the presence of an alkali to the sodium salt of the hydroquinonoid form. This is preferentially absorbed from solution by the textile material during the dyeing operation, and the quinonoid form is subsequently regenerated in the fibre by the action of air or other oxidising agent. During technical processing, it is sometimes necessary to treat cotton materials containing both white and vat dyed parts with hot alkaline liquors of a mildly reducing character. The treatment may result in reduction of the vat dye, and therefore in its partial transference from the originally dyed, to the originally undyed, parts of the material. One of the many factors that together determine the " fastness " of a vat dye on cotton materials is its tendency to cause staining of white cotton under the conditions described. Other things being equal, this tendency should be determined by the ease of reduction of the vat dye, as measured by a redox potential, and the work to be described originated in the attempt to classify vat dyes according to this particular aspect of colour " fastness " by means of potential measurements. In the presence of a sufficient concentration of a strong alkali, the anthrahydroquinone derivative can be assumed to exist in solution entirely in the form of the corresponding bivalent anion, and the equilibrium to be investigated —illustrated for anthraquinone itself—is



The method of investigation adopted consisted in reducing and dissolving the vat dye with sodium hydrosulphite in 0·1 N. sodium hydroxide, and titrating the solution potentiometrically with an oxidising agent in a pure nitrogen atmosphere. The solubility of the oxidised form was always so small that even at very low concentrations precipitation of the quinone occurred shortly after the beginning of the titration. Equilibrium between the solid and liquid phases was sometimes very slow of attainment, and the effects of the non-equilibrium conditions on the potential were often pronounced. In order to increase the solubility of the quinone, and thus delay or prevent its precipitation, pyridine was added in various concentrations to the solution of the reduced vat dye. It was then observed that in the presence of high concentrations of pyridine and of certain other organic solvents oxidation from hydroquinone to quinone occurred in two non-overlapping stages with the intermediate formation of a semiquinone. These observations led to the theoretical and experimental investigation of semiquinone formation by anthraquinone derivatives described in this and the preceding paper. The corresponding equilibria—again illustrated for anthraquinone itself—are

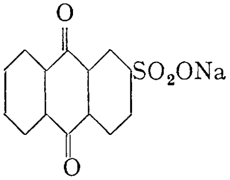


in which the semiquinone is represented as containing an electron shared between the two oxygen atoms.

For a study of semiquinone formation by insoluble anthraquinone derivatives of the vat dye type, an investigation of a soluble derivative, such as the sodium sulphonate, is an obvious preliminary, since the theoretical and practical complications due to the precipitation of the fully oxidised form do not then arise either in purely aqueous solutions or in solutions containing water and miscible organic solvents. The investigation of sodium anthraquinone-2-sulphonate will therefore be described first, followed by that of anthraquinone itself, which will serve to illustrate the general treatment of systems with an insoluble oxidised form. Results will also be given for the three insoluble anthraquinone derivatives: 1-benzoylamino- and 1 : 4-dibenzoylamino-anthraquinones and 1 : 2-anthraquinone-naphthacridone. The first of these, like anthraquinone itself, has no dyeing properties, but the last two are both dyes, and the acridone (marketed as Caledon Red BN) is an important member of the vat group. It is hoped to describe later the results obtained with more complex members of the group.

All the results to be recorded refer to solutions 0·1 N. in sodium hydroxide containing low concentrations of neutral salts, but titrations carried out in the absence of organic solvents will be described as titrations "in water"; when the solution contains an organic solvent, such as pyridine, in addition to water, the titration will be described as having been done in a stated percentage of, for example, pyridine. The experimental results will be analysed by the methods described in the preceding paper, and the symbols, and enumeration of equations, used in that paper will be adopted here.

Sodium anthraquinone-2-sulphonate.



This substance was titrated potentiometrically by Conant, Kahn, Fieser and Kurtz[1] in aqueous buffer solutions. They found that the slopes of the titration curves were greater than the values calculated for a two-electron oxidation of the hydroquinone to quinone, and suggested that this might be due to the formation of a compound of the two.

Fig. 1 shows the curves obtained from titrations in water (A), 50 % aqueous pyridine (B), and 50 % aqueous ethylenediamine (C), all at 25° C. For both curves (B, C) obtained in the presence of an organic solvent the mid-point is a point of inflexion which divides the curve into two similar and well-defined steps corresponding to oxidation in two well-separated stages. Each half of curve C has the theoretical form for a one-electron process, and the individual normal potentials E_1 and E_2 can be calculated from equations (20) and (21). The difference between these two potentials is equal to $2\Delta E$, which is proportional to log K, and the semiquinone formation constant K is readily calculated (equation (10)). When the two one-electron stages are separated as widely as in curves B and C, their normal potentials are given approximately by the points on the curve at $\alpha = 0{\cdot}25$ and $0{\cdot}75$, and it is thus obvious from Fig. 1 that the semiquinone formation constant

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[1] J. B. Conant, H. M. Kahn, L. F. Fieser and S. S. Kurtz, Jr., *J. Amer. Chem. Soc.*, 1922, 44, 1382.

is much greater in the ethylenediamine than in the pyridine solution. In order to show the close agreement between the actual titration curves and the theoretical forms, the experimental data are plotted as points in Fig. 1, whilst the lines are the theoretical curves constructed from the mean values of constants calculated from the data; this applies to all the titration curves reproduced in the paper.

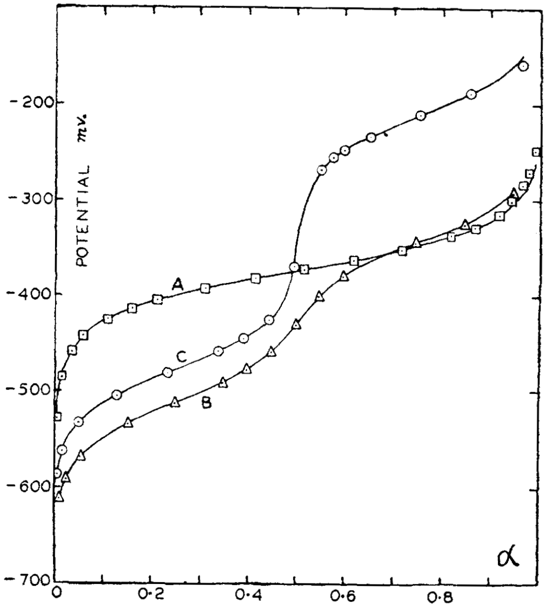


Fig. 1.—Sodium anthraquinone-2-sulphonate at 25° in (A) water, (B) 50 per cent. pyridine, and (C) 50 per cent. ethylenediamine.

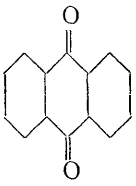
There is no point of inflexion at the middle of curve A obtained from a titration in water, and no superficial evidence of a two-stage process, but—as found by Conant and his co-workers—it is steeper than a simple two-electron curve. Individual experimental points yield concordant values of the semiquinone formation constant calculated from the mid-point potential E_3 by means of equation (23); this concordance is shown by the agreement between the experimental points plotted and the theoretical curve drawn. The values of the constant (values of $\sqrt{K}$ yielded directly by equation (23) will generally be quoted), and those of the normal potentials E_1 and E_2, for the three titrations illustrated are shown in Table I.

TABLE I.

Medium.	$\sqrt{K}$ at 25° C.	E_1 at 25° C. mv.	E_2 at 25° C mv.
Water . . .	1·76	− 389	− 359
50 % Pyridine . .	25·2	− 512	− 346
50 % Ethylenediamine	178	− 478	− 212

The titration curve in water illustrates conditions under which the two one-electron stages of oxidation overlap, the maximum fraction of the substance present in the system as semiquinone (at the mid-point) being 47 % compared with 92·6 % and 98·9 % respectively for the systems containing pyridine and the diamine (equation (18)). It has been shown that a two-stage oxidation is not disclosed by step-formation in the titration curve until $\sqrt{K}$ exceeds 4. Titrations have also been carried out at 50° in 50 % cellosolve (ethyleneglycol monoethylether), in 20 % and 50 % pyridine, and in water. The results show that in all cases a semiquinone is formed as an intermediate product in the oxidation of the hydroquinone, and that the formation constant of the semiquinone is much higher in the solutions containing organic solvents than in purely aqueous solutions. Near the mid-points of the titrations, where the semiquinone concentrations have their maxima, the solutions are brown, a shade that cannot be obtained by a mixture of the colours corresponding to the fully reduced (red) and fully oxidised (almost colourless) solutions. Ethylenediamine itself has pronounced reducing properties, and satisfactory oxidative titrations (against ferricyanide) cannot be made in an ethylenediamine medium at 50° C. A solution of sodium anthraquinone sulphonate in 50 % aqueous ethylenediamine, 0·1 N. in sodium hydroxide, is yellow, but on standing at the ordinary temperature it becomes brown, and this is presumably due to reduction by the solvent to the semiquinone.

Anthraquinone.



Although anthraquinone is only slightly soluble in water, it can be dissolved in 50 % aqueous pyridine at 25° C. or above to yield a 0·001 M. solution (0·002 N. as an oxidising agent). At this concentration, which is a convenient one for titration, well-defined potentials are established, and most of the results described in this paper were obtained by titrating 0·002 N. solutions of the fully reduced anthraquinone derivatives. The titration of anthrahydroquinone itself in 50 % pyridine at this concentration can be made without any precipitation of the quinone, and the same relatively simple conditions prevail as in the titration of the anthrahydroquinone sulphonate. The line in Fig. 2 is drawn through the data obtained in the titration of a 0·002 N. solution in 50 % pyridine at 50° C., and coincides with the theoretical curve constructed for a two-stage oxidation with a $\sqrt{K}$ value of 25·2, agreement being perfect within the experimental errors. Thus the oxidation of anthrahydroquinone itself under these conditions is accompanied by intermediate semiquinone formation. The points plotted in circles in Fig. 2 are the experimental results obtained from similar titrations of anthrahydroquinone in 0·0002 N. solution, and those plotted in squares from one made in 0·00004 N.

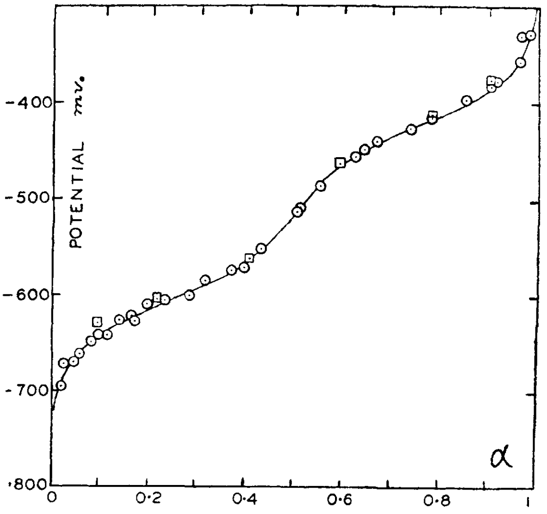


FIG. 2.—Anthraquinone in 50 per cent. pyridine at 50° and concentrations of 0·002 N. (line), 0·0002 N. (circles), and 0·00004 N. (squares).

solution. It is not to be expected that results obtained at these extreme dilutions will be as reliable as those obtained at higher concentrations, but they show no systematic effect of concentration on the form of the titration curve such as would be expected if a compound of higher molecular weight were formed between quinone and hydroquinone.

When the proportion of pyridine in the solvent is lowered considerably below 50 % precipitation of the quinone occurs during the oxidative titration of 0·002 N. anthrahydroquinone solutions—at an earlier stage the lower the proportion of pyridine. Fig. 3 shows curves obtained at 50° C. in 20 % pyridine (A), 10 % pyridine (B), and water (C). These are typical of curves obtained when the quinone is precipitated.

In curve A precipitation does not occur until a late stage, in the neighbourhood of $\alpha = 0·8$. The precipitation is accompanied by a potential break, and a slight fall of potential clearly indicative of non-equilibrium conditions. During the portion of the titration corresponding to α values between 0 and 0·8 no solid phase is present, and, since the stage extends well past the mid-point of the titration, the values of E_1, E_2, E_3 and $\sqrt{K}$ can be obtained by the same simple analysis as that used for the anthraquinone sulphonate in 50 % pyridine or in water. The line drawn over the α range 0 to 0·8, which fits the experimental points, is the theoretical curve constructed for a $\sqrt{K}$ value of 10·1. For such a part of the titration as corresponds to true equilibrium conditions between $\alpha = 0·8$ and 1, the electrode equation (30), or one of its simplified forms, should be applicable. A few trials show that the value of C/KL is less than 0·04, and hence that the approximate equation (35) can be used. The line drawn is the theoretical curve for an E_M value of -469 mv., and it is seen to fit the experimental data for values of α between about 0·9 and 1. Its intersection with the first branch of the curve is at approximately $\alpha = 0·65$, and this is the point at which precipitation of the quinone would begin in the absence of metastable conditions. The experimental points between $\alpha = 0·65$ and 0·8 correspond to systems supersaturated with the quinone, those between $\alpha = 0·8$ and 0·9 to non-equilibrium transition systems, and those between $\alpha = 0·9$ and 1 to systems saturated with the quinone and represented by the theoretical curve as drawn. If this curve were continued back to $\alpha = 0·5$, the corresponding value of the potential would be E_M.

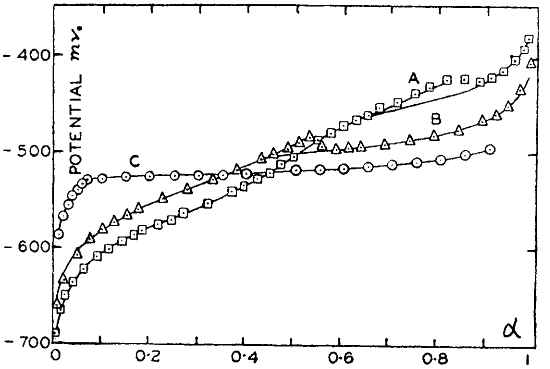


FIG. 3.—Anthraquinone at 50° in (A) 20 per cent. pyridine, (B) 10 per cent. pyridine, and (C) water.

It is clear that the stage of the titration that corresponds to true equilibrium conditions in the presence of solid quinone is rather short to give a very reliable E_M value. It can, however, be used, with equation (41), to calculate the solubility L of anthraquinone in 20 % pyridine at 50° C., since the values of both E_3 and $\sqrt{K}$ are known from the analysis of the first stage of the titration. The solubility calculated in this way is $3{\cdot}4 \times 10^{-4}$ moles/lit., whilst direct solubility measurements yielded the value $3{\cdot}2 \times 10^{-4}$ moles/lit. The satisfactory agreement confirms the theoretical interpretation of the titration data.

Curve B shows similar features to A, but the break occurs very shortly after the mid-point. The stage of the titration prior to precipitation of the quinone is nevertheless sufficiently long for an accurate determination of the constants from equation (23) and the mid-point potential, and the curve drawn to represent this stage is the theoretical curve for a $\sqrt{K}$ value of 6·2. For the later stage of the titration, following precipitation of the quinone, the full electrode equation (30) must be used, and the line drawn is the theoretical curve with a C/KL value of 0·32 When $\sqrt{K}$ is assigned its value of 6·2, C being equal to 0·001 M., the calculated value, L, of the solubility of anthraquinone in 10 % pyridine at 50° C. is 8×10^{-5} moles/lit.; the measured solubility is 7×10^{-5} moles/lit., again in reasonable agreement. Although in this titration precipitation of the quinone did not occur until approximately $\alpha = 0{\cdot}55$, the theory shows that the solution became saturated at an α value of about 0·45.

Curve C in Fig. 3 was obtained by titration in water, and it is of particular interest to know whether semiquinone formation occurs under these conditions, which obtain in the practical application of vat dyes. For a 0·002 N. solution precipitation begins very early (α less than 0·1) and all that can be shown from this short part of the titration is that the electrode equation (37*b*) yields concordant values for the normal potential E_1 of a one-electron process, whilst drifting values are obtained from equation (37*a*) for the normal potential of a two-electron process. As has been shown, this provides evidence of semiquinone formation, and an approximate value of the hydroquinone-semiquinone normal potential E_1, but no evidence on the magnitude of the semiquinone formation constant. It is not to be expected that a very accurate value of E_1 could be obtained from such a short branch of the curve, but the means from six titrations were in reasonable agreement (ranging from — 482 to — 478 mv.). For the branch of the curve following precipitation the electrode equation (30) with a C/KL value of 50 is in good agreement with the experimental data as shown by the theoretical curve drawn in the figure. Since the value of $\sqrt{K}$ is not now known, the solubility L of anthraquinone in water cannot be calculated, but from a direct solubility measurement (3×10^{-6} moles/lit.), and by reversal of the procedure previously adopted, the value of $\sqrt{K}$ is calculated to be 2·6. From this and the value of E_1 determined from the first short branch of the curve, ΔE, E_2, and E_3 may be calculated.

In order to test this analysis of the experimental data, titrations were made in more dilute anthrahydroquinone solutions (*ca.* 0·0005 N.) containing a minimum of pyridine. The object was to add only so much pyridine that precipitation of the quinone from the very dilute solution was delayed sufficiently to permit a complete analysis of the first branch of the titration curve. In 2 % pyridine, precipitation began before the mid-point, but a reasonably accurate value of the mid-point potential yielding concordant values of $\sqrt{K}$ could be obtained by extrapolation. With 3 % pyridine, precipitation also occurred before the mid-point when the titration was carried out slowly, but in a rapid titration precipitation did not begin until after the mid-point, and the values of E_3 and $\sqrt{K}$ could be determined without extrapolation. Under the conditions of rapid titration, the data obtained after precipitation of the quinone had begun were unreliable, but a reliable value of C/KL could be obtained from a slower titration, and from the previously determined value of $\sqrt{K}$ the solubility of anthraquinone in 3 % pyridine at 50° C. could be calculated. The result obtained was $1{\cdot}35 \times 10^{-5}$ moles/lit., which compares satisfactorily with a measured value of $1{\cdot}2 \times 10^{-5}$ moles/lit.

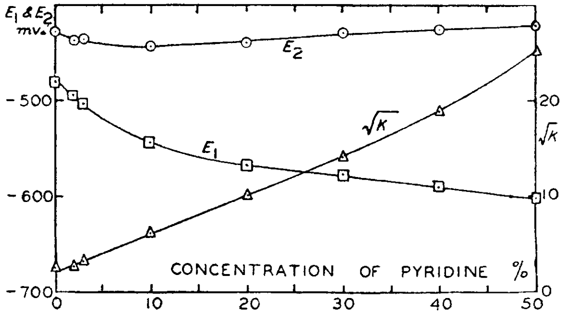


FIG. 4.—Anthraquinone at 50° in various concentrations of pyridine.

The values obtained for $\sqrt{K}$ at 50° C. are plotted in Fig. 4 for different percentages of pyridine in the solvent, ranging from 0 to 50 %, and although the accuracy of the measurement in systems containing little or no pyridine is not high, the value of $\sqrt{K}$ in a purely aqueous medium is clearly not zero, and is approximately 2. The evidence for the formation of a semiquinone in water is conclusive. The variations of E_1 and E_2 with pyridine content are shown in the same figure. The addition of pyridine results in a progressive fall in the normal potential of the oxidation of hydroquinone to semiquinone, but has little effect on the semiquinone-quinone system; hence ΔE, and therefore $\sqrt{K}$, rise progressively with the pyridine content.

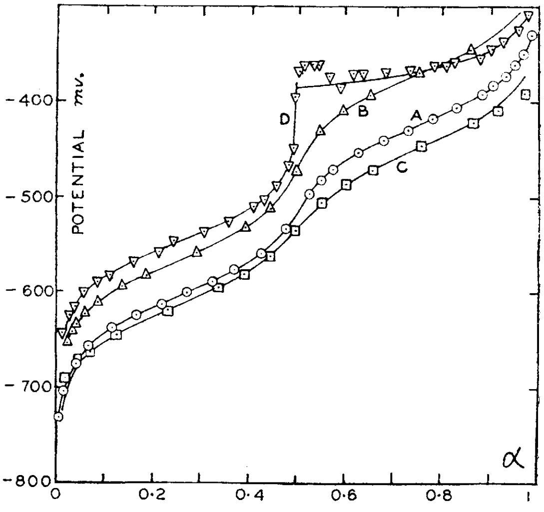


FIG. 5.—Anthraquinone in (A) 50 per cent. pyridine at 50°, (B) 50 per cent. morpholine at 50°, (C) 80 per cent. cellosolve at 50°, and (D) 50 per cent. ethylenediamine at 25°.

Fig. 5 compares the results of titrating 0·002 N. anthrahydroquinone solutions in the following media: (A) 50 % pyridine, (B) 50 % morpholine, (C) 80 % cellosolve, all at 50° C., and (D) 50 % ethylenediamine at 25° C. The lower temperature in the last case was necessitated by the fact that at 50° C. the oxidation of ethylenediamine itself by the titrating solution used (ferricyanide) was disturbingly great. It will be seen that in all these media oxidation occurs in two widely separated stages, the values of $\sqrt{K}$ and of the normal potentials E_1 and E_2 being those shown in Table II. The ability to effect a large increase in the tendency to semiquinone formation is not confined to basic solvents, as shown by the results with cellosolve. The semiquinone formation constant is greatest in the ethylenediamine solution but the figure shows that precipitation of anthraquinone occurred almost immediately following the mid-point of the titration. This is a consequence of the fact that ethylenediamine, unlike pyridine, morpholine and cellosolve, has little solvent action on anthraquinone. For some distance after precipitation had begun non-equilibrium conditions prevailed during the titration in 50 % ethylenediamine, but the data over a short range at the end of the titration are fitted by equation (35) with an E_M value of $-$ 386 mv., and this yields the very low value of 3×10^{-6} moles/lit. for the solubility of anthraquinone in 50 % ethylenediamine at 25° C.

TABLE II.

Medium.		$\sqrt{K}$.	E_1 mv.	E_2 mv.
Water	at 50° C.	2·6	$-$ 480	$-$ 428
50 % Pyridine		25·2	$-$ 602	$-$ 422
50 % Morpholine		34·0	$-$ 566	$-$ 370
80 % Cellosolve		19·4	$-$ 613	$-$ 447
50 % Ethylenediamine at 25° C.		140	$-$ 548	$-$ 294

The defining equation of the semiquinone formation constant ($K = s^2/rt$) shows that if K has only a moderate value, and the solubility of the quinone (t) is very small, s^2/r must also have a very small value; the concentration (s) of the semiquinone must then always be small in relation to that of the hydroquinone (r). These are the conditions that prevail, for example, in the titration of anthraquinone in water, when precipitation of the quinone occurs at a very early stage. When pyridine is added to the system, both the solubility of the quinone and the semiquinone formation constant are increased, and the delayed or prevented precipitation of the quinone is the combined consequence of the two changes. On the other hand, when ethylenediamine is added to the system precipitation of the quinone is delayed solely as a result of an increase in the semiquinone formation constant. This constant acquires such a high value in 50 % ethylenediamine that the amount of quinone formed prior to the mid-point is insufficient to produce the very low concentration existing in a saturated solution of anthraquinone in 50 % ethylenediamine.

For anthraquinone itself and its sodium 2-sulphonate, Table III. compares the normal potentials of the individual stages of oxidation E_1 and E_2 under different conditions of titration, the subscripts A and AS being used to denote the anthraquinone and anthraquinone sulphonate systems, respectively.

It is seen that the effect of sulphonation of anthraquinone on the normal potential E_1 of the oxidation of hydroquinone to semiquinone is almost independent of temperature and medium, and is to produce

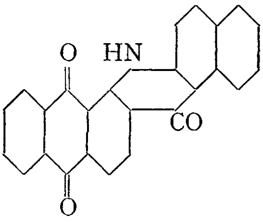
TABLE III.*

		Water.	20 % Py.	50 % Py.		50 % En.
		50° C.	50° C.	50° C.	25° C.	25° C.
$(E_1)_{AS}$	mv.	-412	-495	-532	-512	-478
$(E_1)_A$	mv.	-480	-567	-602	-587	-548
$(E_1)_{AS} - (E_1)_A$	mv.	68	72	70	75	70
$(E_2)_{AS}$	mv.	-362	-367	-368	-346	-212
$(E_2)_A$	mv.	-428	-439	-422	-405	-294
$(E_2)_{AS} - (E_2)_A$	mv.	66	72	54	59	82

* Py = pyridine.
En = ethylenediamine.

a rise of about 70 mv. A similar, but somewhat more variable, effect is produced on the semiquinone to quinone normal potential E_2. These results provide incidental, but substantial, confirmation of the constants calculated from the titration of anthraquinone in water, where —owing to the low solubility of the quinone—the accuracy of the data is not expected to be high. The table also shows that for both substances the addition of pyridine to the aqueous system lowers E_1 considerably, but has only a small effect on E_2, whilst ethylenediamine both lowers E_1 and raises E_2. It is a consequence of this that ΔE, and therefore $\sqrt{K}$, have higher values in the ethylenediamine, than in the pyridine medium.

1 : 2-Anthraquinone-naphthacridone (Caledon Red BN).



This derivative of anthraquinone has nearly twice the molecular weight of anthraquinone itself, and is much less soluble in all the media used in this work. Table IV compares the measured solubilities (moles/lit.) of anthraquinone and Caledon Red BN in water and aqueous pyridine at 50° C. The solubility of Caledon Red BN in 50 % pyridine is only a little higher than that of anthraquinone in water. The reduced form of the vat dye has been titrated (0·002 N. solution) at 50° C. in water, 10 %, 20 %, 30 %, 40 %, and 50 % pyridine, but to preserve clarity Fig. 6 contains only the results of titrations in water (A), 20 % (B) and 50 % (C) pyridine. The curve obtained in 50 % pyridine resembles that yielded by anthraquinone in 50 % ethylenediamine. A semiquinone is formed, and its formation constant is so high that precipitation of the quinone is delayed to the mid-point of the titration.

TABLE IV.

% Pyridine :	0	3	10	20	30	40	50
Anthraquinone :	3×10^{-6}	$1{\cdot}2 \times 10^{-5}$	7×10^{-5}	$3{\cdot}2 \times 10^{-4}$	—	—	$2{\cdot}7 \times 10^{-3}$
Caledon Red BN :	$1{\cdot}1 \times 10^{-8}$	—	$1{\cdot}7 \times 10^{-7}$	$4{\cdot}0 \times 10^{-7}$	$1{\cdot}0 \times 10^{-6}$	$2{\cdot}1 \times 10^{-6}$	$5{\cdot}6 \times 10^{-6}$

At this point 97·7 % of the substance is present as semiquinone, and, on the further addition of oxidising agent, the quinone is almost immediately precipitated. The first half of this titration curve is not significantly altered when the concentration of the dye is diminished from 0·002 N. to 0·0001 N. In 20 % pyridine precipitation of the quinone begins at an α value of about 0·25, and in water almost immediately after the beginning of the titration. A comparison of the experimental points with the theoretical curves drawn in the figure shows clearly the effect of non-equilibrium conditions during the stage of the titration following precipitation, an effect that becomes more pronounced as the solubilities of the anthraquinone derivatives decrease. The potentials are generally too high near the completion of the titrations in the α range 0·9 to 1, an effect that was not pronounced with anthraquinone itself, and is attributable to the fact that the precipitated quinone carries less fully oxidised forms down with it; this deviation becomes still more marked at temperatures below 50° C. The potentials are also too high at the beginning of precipitation, owing to supersaturation, and the titration curve obtained in water shows that the deviation due to this cause can persist over a wide α-range. Nevertheless, there is always a considerable central range over which the curve possesses the theoretical form, and which can be used for the calculation of constants, though the general potential level of this part may be somewhat too high.

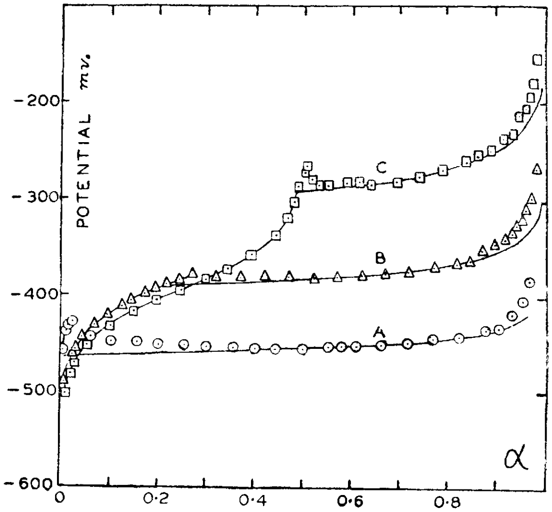


Fig. 6.—Caledon Red BN at 50* in (A) water, (B) 20 per cent. pyridine, and (c) 50 per cent. pyridine.

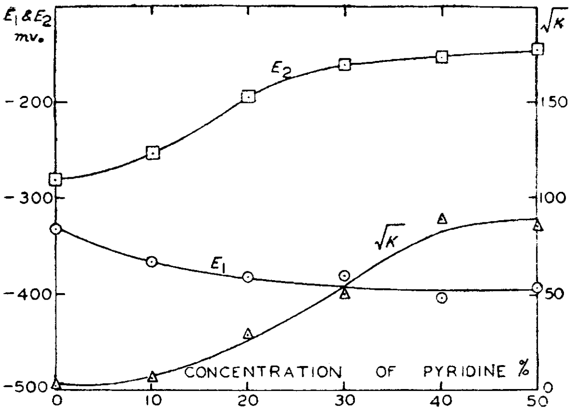
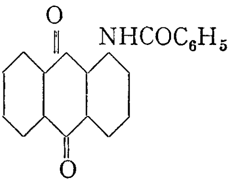


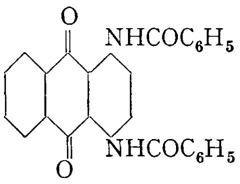
Fig. 7.—Caledon Red BN at 50° in various concentrations of pyridine.

From the first branches of curves B and C accurate E_1 values can be obtained. From curve C, E_3 can be read, and hence $\sqrt{K}$ calculated, but the curve is so steep at the mid-point that considerable uncertainty attaches to the value of E_3 obtained in this way. A more accurate value is obtained from the second branch of the curve by means of the measured solubility of the quinone, and this method must be used for the full analysis of curve B. In the titration in water (A) only a very short branch of the curve is available for the determination of E_1 by the simplified equation (37*b*). The value obtained cannot be very accurate, but with the constants obtained from the second branch of the curve and the measured solubility of the quinone, it yields a $\sqrt{K}$ value of 2·6 for Caledon Red BN in water at 50° C. However approximate this value may be, there is no doubt that it is significantly greater than zero, and that Caledon Red BN, like anthraquinone, forms a semiquinone even in a purely aqueous medium.

Fig. 7 shows the variation of $\sqrt{K}$ at 50° C. with the percentage of pyridine in the solvent, and the simultaneous variations in E_1 and E_2. It is similar to the corresponding Fig. 4 for anthraquinone, but the solvent exerts a greater effect on E_2, and hence on $\sqrt{K}$, in the Caledon Red BN, than in the anthraquinone, system.

1-Benzoylaminoanthraquinone and **1 : 4-Dibenzoylaminoanthraquinone**





When 0·002 N. solutions of the reduced forms of these compounds were titrated in 50 % pyridine the curves showed two widely separated steps indicative of semiquinone formation. At 50° C. no precipitation of the quinone occurred with the mono-substituted anthraquinone, but with the di-substituted product precipitation occurred shortly after the mid-point, its measured solubility being $2{\cdot}2 \times 10^{-5}$ moles/lit. With both products a slight lack of symmetry of the curves about $\alpha = 0{\cdot}5$ or 0·25 suggested that partial hydrolysis of benzoylamino groups occurred under these conditions of reduction and titration; this asymmetry disappeared, or was less pronounced, in titrations at 25° C. and in the presence of a lower concentration of sodium hydroxide (0·05 N.).

In the titration of the mono-substituted derivative in water at 50°C. precipitation occurred at an early stage, and the curve deviated from the theoretical form over a wide α range. An examination of the data by methods already described provided strong evidence of semiquinone formation although no great accuracy could be attached to the constants obtained from the analysis.

No satisfactory data could be obtained from the titration of the di-substituted product in water owing to difficulties connected with hydrolysis of the benzoylamino groups.

Table V compares the values of $\sqrt{K}$ and the normal potentials E_1 and E_2 of the separate one-electron redox stages, for anthraquinone and its three insoluble substitution products in 50 % pyridine at 50° and 25° C. Owing to the high values of $\sqrt{K}$ precipitation of the quinone never occurred before the mid-point of the titration, and these constants are therefore the most accurate obtained in the investigation; a slight uncertainty affects the values for the benzoylamino derivatives at 50° C. on account of their tendency to hydrolysis. The columns headed $(E_1)_S - (E_1)_A$ and $(E_2)_S - (E_2)_A$ contain the differences between the potentials of the substituted product and that of anthraquinone itself and show the effect of substitution on the normal potentials. The values given for 1-benzoylaminoanthraquinone at 25° C. refer to solutions 0·05 N. in sodium hydroxide, the concentration of the alkali being 0·1 N. in all other cases. The introduction of the substituents has raised the semiquinone formation constant of anthraquinone in all cases, the effect being greatest with the dibenzoylamino substitution; the monobenzoylamino and acridone substitutions have approximately equal effects. All the substituents raise both normal potentials, the effect of the second benzoylamino group being somewhat greater than that of the first, but much the greatest effect in this respect is shown by Caledon Red BN.

TABLE V.

Substance.	$\sqrt{K}$.		E_1 mv.		$(E_1)_S-(E_1)$ mv.		E_2 mv.		$(E_2)_S-(E_2)_A$ mv.	
	50° C.	25° C.	50° C.	25° C.	50° C.	25° C.	50° C.	25° C.	50° C.	25° C.
Anthraquinone .	25·2	34·6	−602	−587	—	—	−422	−405	—	—
1-Benzoylamino-anthraquinone	83	117	−574	−560	28	27	−327	−316	95	89
1 : 4-Dibenzoyl-aminoanthra-quinone .	290	360	−534	−502	68	85	−218	−198	204	207
Caledon Red BN	85	—	−393	—	209	—	−145	—	277	—

The values obtained for the semiquinone formation constants and normal potentials in water at 50° C. are compared in Table VI, none being available for 1 : 4-dibenzoylaminoanthraquinone.

TABLE VI.

Substance.	$\sqrt{K}$.	E_1 mv.	E_2 mv.
Anthraquinone . . .	2·6	− 480	− 428
1-Benzoylaminoanthraquinone .	1·7	− 446	− 416
Caledon Red BN . . .	2·6	− 331	− 280

Experimental.

Methods.

The titration vessel was of hard glass provided with a ground glass lid which carried a mercury-sealed stirrer, two electrodes, two burettes, nitrogen inlet- and outlet-tubes, and a connection to a mercuric oxide half-cell. In addition, an inspection tube was provided for examining the deeply coloured solutions of the reduced, or partially reduced, compounds. This consisted of a short length of flattened glass tube with connections to the nitrogen supply and to a vacuum, enabling it to be filled at any time during a titration, and its contents to be returned to the titration vessel after examination. The electrodes consisted of 1·5 cms. of bright platinum wire of S.W.G. 24. The burettes were of 3 c.c. capacity, and could be read to 0·001 c.c. The mercuric oxide half-cell was filled with 0·1 N. sodium hydroxide, and was chosen because the solutions to be titrated were also 0·1 N. in sodium hydroxide. Half-cells were compared with 0·1 N. calomel electrodes using a 0·1 N. potassium chloride bridge, and the potential of the combination was found to be 0·148 volt at 20° C., in agreement with the measurements of Donnan and Allmand.[2] They calculated the potential of the mercuric oxide half-cell to be 0·167 volt at 20° C., and this value has been used in the present work. When the titrations were made in purely aqueous solutions there was no liquid junction potential, but when the solutions contained organic solvents the junction potentials may have been considerable. Since their values were unknown no corrections were made for them, and they are therefore included in the recorded normal potentials. The titration vessel was supported in a thermostat at the required temperature, and the reference half-cell in a separate vessel at 20° C. The potentiometric apparatus gave readings accurate to one millivolt under the least favourable conditions.

The volume of solution titrated was always 200 c.c., 0·1 N. in sodium hydroxide, and usually 0·001 M. (0·002 N.) with respect to the hydroquinone. During the preliminary reduction of the quinone, and the subsequent oxidative titration, a slow current of nitrogen was passed through the apparatus. After the air had been replaced by nitrogen, the quinone was reduced by the addition through a burette of about 2·5 c.c. of 0·2 N. sodium hydrosulphite—a 25 % excess—and the inspection tube was used to ascertain when dissolution of the quinone was complete. The solution was stirred for an hour or more to absorb any remaining traces of oxygen from the gas space, and it was then titrated with a 0·2 N. solution of the oxidising agent; the titre was thus about 2 c.c. With insoluble anthraquinone derivatives in crystalline form, as obtained after purification by crystallisation from an organic solvent, complete dissolution by reduction under the conditions described was an impracticably lengthy process. The weighed quinone was therefore dissolved in a weighed amount (1 c.c) of concentrated sulphuric acid in a small cup of thin glass, the solution poured into water in the titration vessel, the cup dropped in and broken up, and the calculated volume of N. sodium hydroxide run in to neutralise the acid and to make the solution 0·1 N. in alkali when diluted to 200 c.c. Precipitated in this way from sulphuric acid solution, the insoluble quinones were much more easily reduced and dissolved, but the solutions so obtained were 0·09 M. in sodium sulphate. When the solutions contained organic solvents this procedure was generally unnecessary, and the systems titrated were free from neutral salt except the small quantity derived from the sodium hydrosulphite.* 1 : 4-Dibenzoylaminoanthraquinone could not be dissolved in concentrated sulphuric acid and reprecipitated without some decomposition, presumably hydrolysis of the benzoylamino groups, and it is for this reason that no satisfactory titration curves of the compound in water have been obtained.

When sodium hydrosulphite functions as a reducing agent it liberates hydrogen ions, and an alkaline solution was therefore used for reduction such that after oxidation of the hydrosulphite it was 0·1 N. in sodium hydroxide. The oxidising agent generally used for the titration was a

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[2] F. G. Donnan and A. J. Allmand, *J. Chem. Soc.*, 1911, **99**, 845.

* The solutions of Caledon Red BN in 10 %, 20 %, and 40 % pyridine contained sodium sulphate, but titrations in 30 % pyridine indicated that the salt had only a small effect.

neutral potassium ferricyanide solution of analytical purity, but in a few titrations the oxidising agent was phenol indo-2 : 6-dichlorophenol in 20 % pyridine. This latter substance was standardised against pure anthraquinone, and since it has a much lower redox potential than ferri cyanide it may be used with advantage if disturbing non-reversible oxidation processes can occur in the system under investigation, for example, oxidation of the organic solvent.

Materials.

The sodium anthraquinone-2-sulphonate used was a commercial sample. Anthraquinone, its mono- and di-benzoylamino derivatives, and 1 : 2-anthraquinone-naphthacridone (Caledon Red BN) were all purified for this work, and their purity was checked by fractional solvent treatments, or dyeing processes, combined with measurements of absorption spectra.

The pyridine used in many experiments was fractionally distilled and collected over a boiling range of 1° C. It was slowly oxidised by potassium ferricyanide under the conditions of the titrations, but more thorough fractionation, and collection over a boiling range of only 0·2°, effected no alteration in this respect. The cellosolve and morpholine were commercial solvents, and ethylenediamine was used in the form of the aqueous solution supplied commercially; these substances also were oxidised slowly by ferricyanide. Solutions described as 50 % pyridine, morpholine or cellosolve contained 100 c.c. of solvent in 200 c.c. total volume. The commercial ethylenediamine was analysed by weight, and solutions described as 50 % contained 100 g. of the amine in a volume of 200 c.c.

Oxygen-free nitrogen was obtained by forcing cylinder nitrogen through an alundum thimble into the bottom of a 4-foot column of a solution containing 160 g. of sodium hydrosulphite, 150 g. of potassium hydroxide, and 8 g. of sodium anthraquinone-2-sulphonate per litre of water (Kautsky and Thiele [3]), and the purified nitrogen was stored until required over a solution of the same composition. The gas was tested by bubbling through a very dilute (0·0002 N.) solution of anthrahydroquinone in 50 % pyridine in the titration vessel, the solution having been previously titrated until the mid-point was reached and the titration curve was at its steepest. The slow oxidation that occurred during the passage of the nitrogen was followed by the potential changes, and the test demonstrated that the oxygen introduced with the nitrogen during titrations would have no measurable oxidising effect. The amount of oxygen absorbed in this test corresponded to less than 0·0005 % of the gas passed through the solution.

Solubility Measurements.

The solubilities of the quinones in aqueous pyridine were measured by diluting solutions of the quinones in pure pyridine with the required volumes of water, allowing them to stand for long periods in a thermostat to ensure the attainment of equilibrium, filtering, and matching the colours of the filtrates against those of solutions of known concentrations. According to the colour intensity, the observations were made in a colorimeter, in Nessler cylinders, or in longer tubes, and in most cases the quinone solution was first reduced with alkaline hydrosulphite to the tinctorially more intense anthrahydroquinone. For the measurements in water the quinones were boiled with water for ½ to 1 hour, the solutions allowed to stand for many hours in the thermostat, filtered through the finest grade of sintered glass filter, and the filtrates reduced. The solutions so obtained were matched in 6-foot stainless steel tubes with plane glass bottoms against solutions of known concentrations made by diluting

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[3] H. Kautsky and H. Thiele, *Z. anorg. Chem.*, 1926, **152**, 342.

relatively small volumes of standard pyridine solutions of the quinones with large volumes of alkaline hydrosulphite solution. The solubilities of the quinones in water were so small that the colours of the anthrahydroquinones were considerably modified by the blue-green colour of distilled water, but a satisfactory colour match against a suitable standard could generally be obtained, and duplicate measurements gave reasonable agreement.*

Results.

Most of the results have already been given, and some of the titration curves have been illustrated. For checking the reproducibility of the results, and for investigating particular features, a number of the titrations have been repeated several times, and in the titration curves reproduced it has sometimes been impossible to show all the experimental points. The purity of the anthraquinone and its insoluble derivatives was confirmed by the titres, which agreed with the theoretical within the experimental errors when no extraneous oxidation processes occurred. The commercial sample of sodium anthraquinone-2-sulphonate—which was not specially purified for the work—also gave titres in substantial agreement with theory, but a mixture of isomers would not, of course, be revealed in this way.

The concordance between the experimental and theoretical forms of the titration curves has also been illustrated. For the first branch of the curve (no precipitate) the agreement was generally excellent, but the potentials were usually too high at both ends of the second branch (precipitated quinone). The first branch could often be followed appreciably past the point of intersection of the two branches under stable conditions, and when precipitation began the potential then fell only slowly to its equilibrium value. The high potentials at the ends of the second branches are due to the inclusion of reduced forms by the precipitated quinones, the concentrations of the reduced forms in solution thus being below the calculated values. This effect was pronounced when Caledon Red BN was titrated in water at 25° C., especially in the presence of sodium sulphate. The precipitate was much duller in colour than the fully oxidised dye, and the supernatant solution became colourless before the theoretical volume of oxidising agent had been added. Further quantities of the oxidising agent were slowly reduced, and the normal bright shade of the quinone was obtained when the theoretical end-point had been reached. The high potentials obtained under these conditions tend to drift slowly downwards, but it would often require an impracticably long time to reach equilibrium after each addition of the oxidising agent. A high temperature, the absence of neutral salt, and the presence of organic solvent all tend to diminish this effect.

The methods employed for the theoretical analysis of the titration curves have been explained, but that used for the results obtained by the titration of insoluble anthraquinone derivatives in purely aqueous media will be examined more critically. In this case the first branch of the titration curve (no precipitate) is very short. The method used consists in attempting to fit the experimental data by a one- or two-electron equation (equations (37*a*) and (37*b*)). When only the one-electron equation (37*b*) affords a satisfactory fit, the assumption that the oxidation occurs in two stages, and the calculation of an approximate value for the normal potential of the first stage, are justified; the semiquinone formation constant is obtained from the normal potential so calculated together with other constants derived from the second branch of the titration curve and solubility measurements. When the first branch of the curve becomes

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* No great accuracy is required in the solubility measurements since an error of 20 % corresponds with potential changes of only 2·5 and 5 mv., respectively, for bivalent and univalent processes.

very short, a doubt exists as to what significance can be attached to a fit between the one-electron equation and experimental data covering a very short α range; in fact, an approximate fit can sometimes be obtained with either a one- or two-electron equation, and the justification for the whole procedure then requires careful scrutiny.

Table VII gives the experimental values of α and the potential E, prior to precipitation in a titration of anthrahydroquinone in water at 50° C. It also contains for each pair of observations the value of the normal potential E_1 calculated from the one-electron equation (37*b*) corresponding to the oxidation of a hydroquinone to a semiquinone, and that of a normal potential E_3 calculated from the equation (37*a*) and corresponding to oxidation in a single two-electron stage without formation of an intermediate semiquinone.

TABLE VII.

α.	E mv.	E_1 mv. (Semiquinone Formed).		E_3 mv. (No Semiquinone Formed).
0·0096	−592	−476	−480	−524
0·0127	−579	−477		−518
0·0177	−573	−481		−517
0·0228	−566	−481		−514
0·0329	−556	−482		−509
0·0430	−548	−482		−505
0·0582	−540	−484		−501
0·0734	−535	−486		−500
0·0987	−529	−490		−498

These data leave little doubt that at very low values of α the reaction is a one-electron, and not a two-electron, process; the drift in the value of E_1 as α increases is due to the increasing effect of the second stage in the oxidation, of which the normal potential is only 52 mv. higher than that of the first stage.

Table VIII gives similar data for the titration of Caledon Red BN in water. Since this is much less soluble than anthraquinone, the α range available for exploration is much shorter. It would be difficult to decide from these figures alone whether this short part of the titration should be represented as a one-electron process—the drift in E_1 being due to a second, overlapping process—or as a two-electron process, the drift in E_3 being due to initial disturbances or inaccuracies.

TABLE VIII.

α.	E mv.	E_1 mv. (Semiquinone Formed).		E_3 mv. (No Semiquinone Formed).	
0·0010	−502	−329	−331	−406	
0·0025	−478	−331		−395	
0·0050	−458	−330		−384	
0·0100	−440	−332		−376	−377
0·0150	−434	−337		−376	
0·0200	−431	−343		−377	
0·0250	−429	−347		−378	

That the first of these interpretations is the correct one can, however, be shown in the following way. From equation (27), the value of $E_3 - E_M$ for a two-electron oxidation without semiquinone formation would be 32 log . $C/2L$ mv., or in the present case 150 mv. (C = 0·001 M.). This value depends solely upon a solubility measurement. From the titration data—again on the assumption of a two-electron process—E_3 must be approximately equal to − 377 mv. as shown in the above table, whilst E_M, the potential at α = 0·5, is an experimental quantity equal to − 455 mv. in this particular titration (see Fig. 6, A). The "experimental" value of $E_3 - E_M$ is thus 78 mv., or only about half that calculated from the solubility measurement. Detailed examination of the experimental data shows that no probable experimental error is large enough to bring the two values into accord, hence that the fundamental assumption of a two-electron oxidation is fallacious. The intermediate formation of a semiquinone is confirmed, and the calculation of its formation constant from a normal potential approximately equal to − 331 mv. for the oxidation of hydroquinone to semiquinone is justified.

Pyridine and other organic solvents used are slowly oxidised by potassium ferricyanide. The effect is greatest at the highest potentials, and thus at the ends of the titrations, but oxidation of pyridine did not occur to a disturbing extent except in the titration of very low concentrations of the anthrahydroquinones. In these, and some cases when other solvents were used in ferricyanide titrations, it has been necessary to neglect the last portions of the titrations ; phenol indo-2 : 6-dichlorophenol is to be preferred as an oxidising agent for use with these solvents.

The colour changes observed during titrations in 50 % pyridine, when a high proportion of semiquinone was always present at the mid-point, were the following : For anthraquinone itself, the fully reduced solution is red and the fully oxidised nearly colourless, but at the mid-point the solution is brown. Shortly after the mid-point the solution becomes green or brownish green. It was at first thought that the semiquinone was brown and that the green colour might be due to another intermediate compound, possibly similar to the green compound obtained by Scholl [4] and formulated by him as containing two molecules of anthraquinone combined with one of anthrahydroquinone. A substance of this composition would be expected to be formed to the maximum extent at $\alpha = 0{\cdot}67$, which is the neighbourhood in which the green colour is observed. On the other hand the formation of such a substance would necessarily disturb the symmetry of the titration curves, whereas these are in fact symmetrical within the experimental error ; in addition, no effect of total concentration could be detected on the shape of the titration curve (Fig. 2), though it is not certain that the measurements at high dilutions are sufficiently precise to show up such an effect. It is possible that the brown colour observed at the mid-point is due to a mixture of green semiquinone with the red hydroquinone still present in a relatively low concentration, and that as the oxidation progresses the green becomes clearer owing to the replacement of the hydroquinone by the almost colourless quinone. Sodium anthraquinone-2-sulphonate is also red in the fully reduced, and nearly colourless in the fully oxidised form, whilst the colour of the solution is brown at the mid-point, but no green colour has been observed.

For 1-benzoylaminoanthraquinone, the fully reduced colour is bluish red, the fully oxidised golden brown or yellow, whilst at the mid-point the colour of the solution is deeper and dull brown. When 1 : 4-dibenzoylaminoanthraquinone is reduced in a purely aqueous medium the colour of the solution is violet, but in 50 % pyridine it is a dull bluish green. This changes to reddish-brown at the mid-point of the titration and to bluish-red after completion of the oxidation.

Summary.

Redox titrations are described of anthraquinone, sodium anthraquinone-2-sulphonate, 1- and 1 : 4-benzoylaminoanthraquinones and Caledon Red BN (anthraquinone-1 : 2-naphthacridone) these substances being reduced to the soluble leuco-compounds and titrated with an oxidising agent. Titrations have been made in purely aqueous solutions and in solutions containing pyridine or certain other organic solvents. It is found in every case that oxidation takes place in two stages, with the formation of a semi-

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[4] R. Scholl and O. Böttger, *Ber.*, 1930, **63**, 2120.

quinone as a soluble intermediate compound. Semiquinone formation is promoted by the addition of the organic solvents to the solutions, and by the presence of the benzoylamino and naphthacridone groups; the sulphonate group has little effect on semiquinone formation but raises the normal potentials of each stage of the oxidation.

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