899. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XV.* Some New 3 : 3'-Disubstituted Naphthidines.*

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The redox properties of a number of new 3 : 3'-disubstituted naphthidines and their applications as analytical reagents have been examined. Spectrophotometric data for the oxidised naphthidines, sensitivities towards oxidants, and transition potentials are given for the reactive compounds. Their behaviour as indicators in several conventional titrations is described.

It has been shown that naphthidine[1] and 3 : 3'-dimethylnaphthidine[2] can be used advantageously as reversible chemical indicators in certain redox titrations. The dimethyl derivative was found to be about ten times as sensitive to oxidants as the parent base, and its oxidised form was considerably more stable than that of naphthidine. We have now examined several substituted naphthidines in an attempt to correlate their redox properties with the nature of the substituent group. A range of substituted naphthidines having, in the 3- and 3'-position, the groups Et, Pr^n, Pr^i, OMe, Ph, NO_2, NH_2, and SO_3H, has been prepared[3] and their properties of interest in analytical processes are described. The redox properties of these new compounds have been studied spectrophotometrically and potentiometrically, and a comparison has been made with established indicators to assess their suitability for some practical applications.

Colour Reactions and Sensitivity Tests.—In aqueous acid solutions of many oxidants, naphthidine and substituted naphthidines undergo reversible oxidation to highly coloured soluble substances of varying stability. The colour reactions observed with the series under consideration are summarised in Table 1.

Table 1.

Reagent, R =	Colour change, Colourless to:	Reagent, R =	Colour change, Colourless to:
H	Bordeaux red	Ph	Violet
Me, Et, Pr^n, Pr^i, SO_3H	Purple-red	NO_2	No apparent reaction
OMe	Greenish-blue	NH_2	Transient green, brown ppt.

(Here and in subsequent Tables, the naphthidine is represented by the substituent R in the 3- and the 3'-position.)

3 : 3'-Dinitronaphthidine is not oxidised by any common inorganic oxidant, including perchloric acid solutions of cerium(IV). The diamino-derivative is extremely sensitive to oxidants but is probably oxidised, unlike other naphthidines, to a dinaphthadiquinone. The disulphonic acid is oxidised to a stable coloured product only in acid solutions more concentrated than 2M. The sensitivities of the reactive naphthidines to various oxidants have been determined in 0·1N-hydrochloric acid. The low solubility of the free amines in water made it necessary to confine the measurements to solutions in acid. Oxidation at low concentrations of oxidants was slow and might easily be confused with aerial oxidation of the amines, so that a limiting reaction time was necessary in determining the sensitivities. The minimum amount of oxidant detected within two minutes of mixing is given in Table 2.

The diphenyl and dimethoxy-derivatives have slightly lower sensitivities than the dialkyl derivatives, all of which have the same sensitivity towards the oxidants used. In this comparison the disulphonic acid is at a disadvantage because it is oxidised to a stable coloured product only in solutions of acidity 2M or greater, in which the sulphonic acid

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* Part XIV, *J.*, 1958, 2336.

[1] Belcher and Nutten, *J.*, 1951, 548.

[2] Belcher, Nutten, and Stephen, *J.*, 1951, 1520, 3444.

[3] Belcher, Lyle, and Stephen, *J.*, 1958, 3243.

groups are presumably un-ionised. The higher sensitivity towards iron(III) in 0·1N-acid than to other ions can then be explained through ferric ions' acting as electron-acceptors for the ionised sulphonic acid groups, as does the hydrogen ion at high acid concentrations.

TABLE 2.

Reagent, R =	Identification limit (μg.) in 2 ml. of solution.							
	$Cr_2O_7^{2-}$	IO_3^-	$S_2O_8^{2-}$	VO_3^-	$Fe(CN)_6^{3-}$	IO_4^-	Fe^{3+}	OCl^-
H	2	0·8	60	20	0·9	10	—	0·9
Me, Et, Pr^n, Pr^i ...	0·2	0·2	2	1	0·1	0·1	1	0·1
OMe	0·2	0·5	10	1	0·1	0·2	1	0·1
Ph	0·2	0·8	2	1	0·1	0·6	1	0·1
SO_3H	—	—	—	30	20	20	1	0·9

Spectrophotometric Measurements.—The coloured oxidised naphthidines are generally sufficiently stable for absorption spectra to be plotted in the visible region. The spectra of the oxidised naphthidines are independent of the oxidant used, but an increase in acid concentration causes a slight shift of maximum absorption to longer wavelengths (Table 3) and produces a visible change in colour. A quantitative comparison of the colour stability of the oxidised naphthidines under standardised reaction conditions has been made; by observing the change in optical density at the wavelength of maximum absorption during 5—6 hours, the dialkyl- and diphenyl-substituted naphthidines are shown to have similar stabilities, the decrease in optical density being 0·025 to 0·045 for solutions of optical densities 0·2 to 0·8. In contrast, oxidised naphthidine solutions under the same conditions were decolorised completely within 10 minutes and the dimethoxy-derivative within 20 minutes. At acidities above 4M, the disulphonic acid gave colours which were about half as stable as those of the dialkyl derivatives. The optical densities of 1% solutions of the oxidised amines for a path length of 1 cm. ($E^{1\%}_{1\,\mathrm{cm.}}$) were then determined. Results were reproducible for replicate determinations using the same oxidant, different oxidants, and varying amounts of amine. Variation in the strength of sulphuric acid (0·5—4M) gave the same calculated $E^{1\%}_{1\,\mathrm{cm.}}$ values within the experimental error (±20). The molecular extinction coefficients (ε) of the oxidised naphthidines have been calculated from the $E^{1\%}_{1\,\mathrm{cm.}}$ values on the assumption that oxidation does not significantly affect the molecular weights.

TABLE 3. *Spectrophotometric properties of oxidised naphthidines.*

Reagent, R =	$\lambda_{max.}$ (mμ) in M-H_2SO_4	$\lambda_{max.}$ (mμ) in 4M-H_2SO_4	$10^{-3}\varepsilon$
H	530	535	29
Me	550	560	30
Et	550	560	30
Pr^n	550	560	31
Pr^i	550	560	26
OMe	615	—	—
Ph	570	575	21
SO_3H	—	560	—

These oxidised naphthidines have similar absorption bands in the visible region and therefore their molecular extinction coefficients may be taken as a measure of their sensitivities towards oxidants. The low value for 3 : 3′-diphenylnaphthidine is supported by its lower sensitivity (Table 2) towards oxidants. This naphthidine might be expected to have a larger molecular extinction coefficient than dialkylnaphthidines through conjugation of the phenyl and the naphthalene nucleii. That this is not so suggests that coplanarity of the phenyl groups with the oxidised naphthidine nucleus is sterically prevented. Steric effects may also be partially responsible for the greater stability of the coloured oxidised 3 : 3′-disubstituted naphthidines than of naphthidine; the substituents could have a shielding effect on the sensitive oxidised amino-groups. The instability of oxidised 3 : 3′-dimethoxynaphthidine to light of wavelength near its absorption maximum prevented its being included in this study.

Measurement of Oxidation Potentials.—Belcher, Nutten, and Stephen[4] described the determination of the oxidation potentials of naphthidine, its 3 : 3′-dimethyl homologue, and their sulphonated derivatives, but they found that the oxidised naphthidine and its sulphonated product were too unstable for such work. As an alternative, they determined the potentials at which colour formation was first observed (transition potentials). Stockdale,[5] in his comparative study of indicators for the iron(II)–dichromate titration, as well as determining the transition potentials, determined the potentials of maximum colour formation. The latter is an important property since, together with the transition potential, it determines the potential range over which the indicator is progressively oxidised or reduced in a given redox system. The transition potentials of the present series of naphthidines were initially determined for the Fe^{2+}–Fe^{3+} and $Cr_2O_7^{2-}$–Cr^{3+} systems, with diphenylamine-4-sulphonic acid as a control. The greenish-blue colour of dimethoxynaphthidine on oxidation excluded it from this series of measurements. On adding an excess of dichromate to an acid solution of a naphthidine, it was found that the colour did not develop markedly until a few drops of a ferrous iron solution were added, a phenomenon previously observed with diphenylamine.[6] Because of these factors and the complicated non-reversible reduction of dichromate to chromic ions,[7] the transition measurements were repeated in the Fe^{2+}–Fe^{3+} and the Ce^{4+}–Ce^{3+} system. The results for both series of measurements are recorded in Table 4 for various concentrations of sulphuric acid.

TABLE 4. *Transition potentials* (±0·01 v) *at* 20°, *referred to the standard hydrogen electrode.*

Indicator, R =	Acid concentration (M) (H_2SO_4)				
	0·1	0·5	1·0	2·0	4·0
H	0·80	0·81 (0·79)	0·79 (0·79)	0·78 (0·76)	0·76 (0·74)
Me	0·69	0·71 (0·70)	0·71 (0·70)	0·71 (0·70)	0·70 (0·67)
Et	0·70	0·72 (0·72)	0·72 (0·71)	0·72 (0·72)	0·72 (0·69)
Pr^n	0·70	0·72 (0·72)	0·72 (0·71)	0·72 (0·72)	0·72 (0·69)
Pr^i	0·73	0·75 (0·74)	0·75 (0·74)	0·75 (0·74)	0·74 (0·72)
Ph	0·75	0·76 (0·76)	0·76 (0·76)	0·76 (0·75)	0·76 (0·73)
SO_3H	—	— (0·86)	0·83 (0·86)	0·83 (0·85)	0·83 (0·85)
OMe	—	(0·74)	(0·74)	(0·73)	(0·70)

(Values in parentheses are those for the Fe^{2+}–Fe^{3+} and the Ce^{4+}–Ce^{3+} systems.)

Replacement of dichromate by ceric ions as oxidant gave slightly lower values for the transition potentials. The inductive effect of ferrous ions in the dichromate–chromic system was not observed in ceric–cerous systems containing naphthidines. It has been suggested[6] that the ferrous iron is momentarily oxidised to a higher unstable oxidation state which is responsible for the rapid oxidation of the indicator. It seems more likely that an unstable intermediate reduction product in the dichromate–chromic system, perhaps quinquevalent chromium, is responsible.[7]

The observed order (Table 4) for the transition potentials is $SO_3H > H > Ph > Pr^i > OMe > Pr^n, Et > Me$ at each acid concentration and for each inorganic redox system investigated. It is probable that both electronic[8] and steric effects are largely responsible for the observed values, but as yet the information obtained is not sufficient to allow the relative importance of these effects to be estimated.

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[4] Belcher, Nutten, and Stephen, *J.*, 1952, 3857.

[5] Stockdale, *Analyst*, 1950, **75**, 150.

[6] Kolthoff and Sarver, *J. Amer. Chem. Soc.*, 1930, **52**, 4181.

[7] Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, 3rd edn., 1952, p. 466.

[8] Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5204.

Stockdale did not indicate how he determined the potential at maximum development of colour. In this work, the indicator solution containing iron(II) was oxidised with either a dichromate or a ceric solution and the colour intensity compared visually with that of a similar solution in which the indicator was fully oxidised; the oxidation potential was then measured when maximum colour formation had taken place. The potentials were the same for both oxidants within the estimated experimental error (±0·01 v), and the value found for diphenylamine-4-sulphonic acid was the same as that found by Stockdale. Results are in Table 5.

The potential range within which the colour change of the indicators took place in M-sulphuric acid (transition interval) was obtained by subtracting the mean value of the transition potential (Table 4, column 4) from the appropriate potential of maximum colour intensity. It is probable that the indicator solubility plays a part in determining the "transition interval." The more soluble sulphonic acids have appreciably lower ranges than other substituted naphthidines. This is supported by Stockdale's results for diphenylamine and *NN*′-diphenylbenzidine which theoretically should have the same transition potential but have different potentials of maximum colour intensity (0·86 and 0·94 v, respectively). Further support is provided by potentiometric titration of dimethylnaphthidine in a mixture of 50% aqueous acetic acid and 4M-sulphuric acid. A two-electron change is involved in the oxidation to the stable purple-red compound and the "transition interval" is only 0·05 v. This suggests that an indicator having an oxidation potential lower than that corresponding to the equivalence point in a redox titration may still function satisfactorily if its solubility is not too great.

TABLE 5 *Potentials (in volts, referred to the hydrogen electrode) of maximum colour intensity at* 20°.

Indicator, R =	*	H	CH_3	C_2H_5	C_3H_7	C_3H_7	OCH_3	C_6H_5	SO_3H
Potential	0·91	0·83	0·85	0·90	0·90	0·91	0·88	0·94	0·91
Transition interval...	0·09	0·04	0·14	0·18	0·18	0·16	0·14	0·18	0·06

* Diphenylamine-4-sulphonic acid.

Analytical Applications.—Straka and Oesper [9] recommended naphthidine as an internal indicator in the titration of iron(II) with dichromate. Although the colour change is reversible, the indicator response is sluggish and the colour less stable than that of the conventional indicator, diphenylamine-4-sulphonic acid. The main disadvantages of the latter are its dependence on acid concentration and its high "blank" values. Kolthoff and Sarver [10] recommended that it be used only in 0·25—3N-acid. Naphthidine-3 : 3′-disulphonic acid, while oxidised in the same potential range (Tables 4 and 5), functions at higher acid concentrations and gives lower "blank" values. A comparison between the two compounds as indicators in this titration showed that naphthidinedisulphonic acid was a satisfactory indicator in 4—12M-acid, giving end-points to within one drop of 0·1N-dichromate and indicator "blank" values from one-half to two-thirds of those obtained with diphenylamine-4-sulphonic acid in 0·5—2M-acid. The naphthidinedisulphonic acid does not function in this titration in the presence of phosphoric acid. It may be of use as an internal indicator in vanadatometric procedures in which high acid concentrations are often necessary.[11]

New and improved indicators have been recommended for the titration of zinc and cadmium with ferrocyanide in the presence of ferricyanide. A comparison has been made between the naphthidines in titrations of this type under the conditions used by Belcher, Nutten, and Stephen.[2] Although satisfactory, they showed no marked advantages over 3 : 3′-dimethylnaphthidine. Naphthidinedisulphonic acid does not function under the titration conditions.

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[9] Straka and Oesper, *Ind. Eng. Chem.*, *Analyt.*, 1934, **6**, 405.

[10] Kolthoff and Sarver, *J. Amer. Chem. Soc.*, 1931, **53**, 2906.

[11] P. Rao, Murty, and G. Rao, *Z. analyt. Chem.*, 1955, **147**, 161.

In the titration of cadmium with ferrocyanide, the new dialkyl- and dimethoxynaphthidines gave end-points as satisfactory as did 3 : 3′-dimethylnaphthidine, but with no marked advantages. The diphenyl and disulphonic acid derivatives were unsatisfactory, the former because of a sluggish colour-formation and the latter because of its colour-instability.

EXPERIMENTAL

Indicator Solutions.—A 0·2% aqueous solution of disodium naphthidinedisulphonate and 0·2% solutions of the other naphthidines in glacial acetic acid were used.

Oxidising Agents.—Stock solutions of $Cr_2O_7^{2-}$, IO_3^-, IO_4^-, $S_2O_8^{2-}$, VO_3^-, $Fe(CN)_6^{3-}$, Fe^{3+}, and OCl^- were prepared containing 1 mg. of the required ion per ml. Weaker solutions were made by dilution of the stock solution. The oxidants were of " AnalaR " purity except the hypochlorite.

Sensitivity Tests.—1 ml. of the neutral oxidant solution and 1 ml. of 0·2N-hydrochloric acid were added to a small test-tube (3″ × ⅜″ diameter), followed by 1 drop of the organic reagent solution, and the whole was mixed. The oxidant concentration in the test solution was reduced until there was no longer any response from the reagent within 2 minutes of mixing. Blank tests, in which the oxidant was replaced by distilled water, were run concurrently.

Absorption Spectra.—0·2 ml. of a solution of the naphthidine in glacial acetic acid (1—1·5 g./l.) was mixed with 75 ml. of M-sulphuric acid. A slight excess of N-hypochlorite was added and the volume made up to 100 ml. After the colour had fully developed, the absorption spectrum was measured with a Unicam S.P. 600 spectrophotometer. $E^{1\%}_{1\,\mathrm{cm.}}$ values at $\lambda_{\max.}$ were obtained to provide the ε values given in Table 3.

Transition Potentials.—The apparatus, reagents, and procedure have been described in Part XI.[12]

Potentials of Maximum Colour Development.—To each of two 250-ml. beakers, 5 ml. of 0·1N-iron(II) solution in M-sulphuric acid, 95 ml. of the same acid, and two drops of the required indicator solution were added. One of the solutions was then oxidised fully with the selected oxidant. This solution was used for comparison, the potential of the other being gradually raised, first with 0·1N-, then 0·01N- or 0·001N-oxidant, until the colour had developed to the same extent; the potential was then noted.

Direct Titration of Dimethylnaphthidine.—The weighed amount (10—15 mg.) of pure amine was dissolved in warm acetic acid (50 ml.), and 4M-sulphuric acid (50 ml.) was added. The solution was cooled and titrated potentiometrically with standard 0·1N-cerium(IV).

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[12] Belcher, Nutten, and Stephen, *J.*, 1952, 3861.