

825. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XVI.* Anthranilic, Orthanilic, Benzidine-3,3'-dicarboxylic, and Benzidine-3,3'-disulphonic Acids as Redox Indicators.*

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The redox properties of anthranilic, orthanilic, benzidine-3,3'-dicarboxylic, and benzidine-3,3'-disulphonic acids are described. These compounds undergo reversible oxidation in acid solution and orthanilic and benzidine-3,3'-disulphonic acids are shown to be suitable redox indicators for the titration of iron(II) with cerium(IV); very sharp end points (colourless to yellow) are obtained. Evidence is given that anthranilic and orthanilic acids are oxidised *via* benzidine-3,3'-dicarboxylic and benzidine-3,3'-disulphonic acids, respectively.

BENZIDINE-3,3'-DISULPHONIC, benzidine-3'-sulphonic, and benzidine-2,2'-disulphonic acid have been examined as colorimetric reagents for a variety of oxidants.¹⁻³ The first two compounds form greenish-blue merquinoid compounds with a large number of oxidants in acetic acid solutions of pH 2—3 while the last reacts only with the more powerful oxidants. We have found that benzidine-3,3'-disulphonic acid and benzidine-3,3'-dicarboxylic acid undergo instantaneous reversible oxidation, as is to be expected in this type of system,⁴ and can therefore be employed as indicators in certain redox titrations. Anthranilic and orthanilic acids also have redox properties, and the evidence now recorded indicates that they are oxidised *via* benzidine-3,3'-dicarboxylic acid and benzidine-3,3'-disulphonic acid, respectively. These two compounds are the only simple aniline derivatives whose redox properties make them suitable as redox indicators. The use of anthranilic acid as a gravimetric reagent is of course well known⁵ but no account of its redox properties or those of orthanilic acid has been reported previously.

Colour Reactions.—Rather unstable bright yellow colours are formed when the four compounds are oxidised in acid solutions. Although the yellow colours develop more rapidly the lower the acidity of the solution, the stability of the colour is, however, greater at higher concentrations of acid. In warm solution, however, rapid development of colour also occurs at the higher acidities. Benzidine-3,3'-disulphonic acid gives the most stable oxidation product especially in 4M-sulphuric acid solution, the colour being stable for over 2 hr. Since the yellow oxidised products are, with the exception of benzidine-3,3'-disulphonic acid in 4M-sulphuric acid solution, too unstable for the adsorption spectra to be plotted, only the λ_{\max} values could be recorded. These were 445 m μ in all cases.

The similarity in the colours of the oxidation products indicates that the oxidation products of anthranilic and benzidine-3,3'-dicarboxylic acids are the same, and similarly for those of orthanilic and benzidine-3,3'-disulphonic acids. Further evidence that the two simple amines are oxidised *via* the corresponding benzidine derivatives is to be found in the various observations given below.

Transition Potentials.—Measurements were carried out only in the cerium(IV)–iron(II) system, since the poor colour contrast obtained in the dichromate–iron(II) system was not sufficiently sharp to give accurate measurements of the transition potentials. The results obtained are given in Table I.

* Part XV, *J.*, 1958, 4454.

¹ Buscoróns and Nieto, *Anales real Soc. españ. Fís. Quím.*, 1954, **50**, B, 447 (*Chem. Abs.*, 1955, **49**, 771g).

² Buscoróns and Nieto, *Anales. real Soc. españ. Fís. Quím.*, 1954, **50**, B, 455 (*Chem. Abs.*, 1955, **49**, 772a).

³ Buscoróns and Nieto, *Analyt. Chim. Acta*, 1956, **14**, 401.

⁴ Belcher, Nutten, and Stephen, *J.*, 1958, 2236.

⁵ Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand Co. Inc., 1947.

The transition potentials of benzidine-3,3'-dicarboxylic and benzidine-3,3'-disulphonic acids are the highest recorded for simple benzidine derivatives. The high transition potential (1.08 v) hitherto ascribed to *N*-phenylanthranilic acid⁹ has recently been found to be erroneous.¹⁰ It is seen that, as with diphenylaminesulphonic acid and naphthidinedisulphonic acid,¹¹ the transition potentials shift to lower values with increasing acidity. The close agreement in the values is again evidence that the two simple amines are oxidised *via* the corresponding benzidine derivatives to give the same respective oxidation products.

Application as Redox Indicators.—The oxidation of the four acidic compounds in acid solution is reversible. With the majority of simple benzidines, the process is too slow to allow their use as satisfactory indicators; this is the case with the alkoxybenzidines.⁶ However, the redox properties of the present compounds, like those of certain other redox indicators,¹¹ are influenced appreciably by induced oxidations. Thus, in particular redox titrations, the colour change is instantaneous and the reaction is quite reversible, whereas a somewhat slower development of colour is observed when the organic compounds are treated only with an oxidising agent. The present compounds thus have properties which make them suitable for study as redox indicators.

TABLE 1. *Transition potentials at 18–20°, referred to the standard hydrogen electrode.*

Indicator	H ₂ SO ₄ concentration (M)			
	0.5	1.0	2.0	4.0
Anthranilic acid	0.94	0.94	0.92	0.94
Benzidine-3,3'-dicarboxylic acid	0.93	0.92	0.92	0.90
Orthanilic acid	0.93	0.90	0.90	0.88
Benzidine-3,3'-disulphonic acid	0.91	0.90	0.88	0.88

TABLE 2. *Titration of iron(II) with cerium(IV) [ml. of 0.1N-cerium(IV)]*

Indicator	H ₂ SO ₄ concentration (M)				Calc. value
	0.5	1.0	2.0	4.0	
Anthranilic acid	20.07	20.06	20.06	20.05	20.00
Benzidine-3,3'-dicarboxylic acid	20.01	20.02	20.02	20.02	20.00
Orthanilic acid	20.01	20.01	20.01	20.01	20.00
Benzidine-3,3'-disulphonic acid	19.98	19.98	19.98	19.98	20.00
Ferrioin	20.01	20.01	20.00	20.02	20.00

Titration of Iron(II) with Cerium(IV).—The results obtained in the various molar concentrations of sulphuric acid, together with those when ferrioin is used for comparison, are given in Table 2. In all titrations there is a faint yellow coloration before the end-point but this does not obscure the bright yellow colour of the end-point whose appearance is very sharp in all cases. The end-points with anthranilic and benzidine-3,3'-dicarboxylic acids are not quite as sharp as those obtained with orthanilic and benzidine-3,3'-disulphonic acid; the colours fade after a little time but reversal of the end-point is possible 3 or 4 times if done immediately, without altering the result, but the brightness of the colour fades somewhat after each reversal. The results show that over-titration occurs when anthranilic acid is used.

Titration of Iron(II) with Dichromate.—The results obtained, together with those with diphenylaminesulphonic acid, are given in Table 3. An end-point is observed with anthranilic acid only if the colour is compared with an untitrated solution, the change being from blue to the first trace of green. The two benzidine compounds give sharp end-points but the colour change is not very satisfactory, being from blue to green-yellow. Orthanilic acid behaves in the same manner as benzidine-3,3'-disulphonic acid except that no end-point can be detected in solutions weaker than in 2M-sulphuric acid. A very poor colour change was obtained with orthanilic acid in 2M- and 4M-sulphuric acid solutions. But when the yellow colour was reduced with a few drops of iron(II) solution, a sharp end-point, similar to that obtained with benzidine-3,3'-disulphonic acid, was then obtained

⁶ Rees and Stephen, *Talanta*, 1959, **2**, 361.

on addition of more dichromate. This is again evidence that the oxidation of the simple amines proceeds through the corresponding benzidine derivatives.

Titration of Dichromate with Iron(II).—The use of benzidine-3,3'-disulphonic acid as a suitable indicator for this titration has already been reported.¹⁰ It gives a sharp colour change from yellow-green to green in 0.5–4M-sulphuric acid solutions. The results obtained in the various molar concentrations of sulphuric acid, together with those with ferroin, are given in Table 4.

Titration of Oxalate with Cerium(IV).—Orthanilic and benzidine-3,3'-disulphonic acid function as good indicators in this titration at room temperature in the presence of manganous sulphate. No end-points could be obtained with either of these compounds or with ferroin in the absence of any catalysts at 60° or with iodine monochloride as catalyst.

TABLE 3. *Titration of iron(II) with dichromate (ml. of 0.1N-dichromate).*

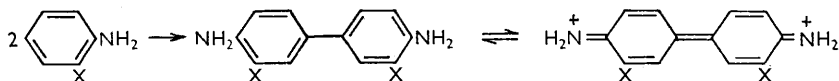
Indicator	H ₂ SO ₄ concentration (M)				Calc. value
	0.5	1.0	2.0	4.0	
Anthranilic acid	—	—	—	—	
Benzidine-3,3'-dicarboxylic acid	19.99	19.99	19.99	19.99	20.00
Orthanilic acid	—	—	20.06	20.06	20.00
Benzidine-3,3'-disulphonic acid	20.04	20.02	20.01	20.01	20.00
Diphenylaminesulphonic acid	20.04	20.03	19.99	—	20.00

TABLE 4. *Titration of dichromate with iron(II) [ml. of 0.1N-iron(II)].*

Indicator	H ₂ SO ₄ concentration (M)				Calc. value
	0.5	1.0	2.0	4.0	
Benzidine-3,3'-disulphonic acid	20.01	19.98	19.99	19.93	20.00
Ferroin	19.97	19.98	19.97	19.97	20.00

The recommended procedure for ferroin states that the temperature must be kept between 45° and 50° throughout the titration:¹² this is not really practicable. The procedure outlined in the experimental section gave very good results. An average of 19.98 ± 0.05 (theoretical = 20.00) was obtained from 6 titrations from accurately weighed separate quantities of sodium oxalate.

Mechanism of the Oxidation of Anthranilic and Orthanilic Acids.—The results recorded above indicate that anthranilic and orthanilic acids, when used as indicators, are probably oxidised *via* the corresponding benzidine derivatives in the following manner:



Polarographic studies gave a curve for anthranilic acid having an $E_{\frac{1}{2}}$ value of 0.25, and on calculation a value of 1.6 for n (the number of electrons involved in the oxidation). A 2-electron change is required if anthranilic acid oxidises *via* the benzidine derivative to the coloured holoquinoid structure.

More conclusive proof for the proposed mechanism was the observation of a spot having the same migration rate and colour reaction as benzidine-3,3'-dicarboxylic acid on subjecting an oxidised solution of anthranilic acid, after its reduction and deionisation, to paper electrophoresis. Electrophoresis of oxidised orthanilic acid did not, however, indicate a spot corresponding to benzidine-3,3'-disulphonic acid, probably because the oxidation of appreciable amounts of this substance follows a different course from that which is evident when the substance is used as an indicator.

EXPERIMENTAL

Indicator Solutions.—0.5% Solution in water containing a small quantity of ammonia.

Development and Stability of Colour.—5 Drops of the indicator solution were mixed with 100 ml. of 0.5–4M-sulphuric acid solution, followed by 1 drop of 0.1N-ceric sulphate solution. A Unicam S.P. 600 spectrophotometer was used.

Transition Potentials.—The apparatus, reagents, and procedure have been described.⁶

Titrations.—The solutions and titration procedures have already been described.⁷

Titration of Iron(II) with Cerium(IV) and Dichromate.—One drop of benzidine-3,3'-dicarboxylic or benzidine-3,3'-disulphonic acid solution, 2 drops of anthranilic acid, and 5 drops of orthanilic acid indicator solutions were used.

Titration of Dichromate with Iron(II).—20 ml. of 0.1N-dichromate solution were acidified with 50% sulphuric acid to give the required acid content at the end of the titration, and diluted with about 80 ml. of water. One drop of the benzidine-3,3'-disulphonic acid indicator solution was added and the mixture was titrated with 0.1N-iron(II) solution to the yellow-green to green colour change.

Titration of Oxalate with Cerium(IV).—To 20 ml. of 0.1N-sodium oxalate solution (or about 0.1340 g. of sodium oxalate dissolved in 20 ml. of water) were added 25 ml. of a 10% aqueous manganous sulphate solution and 1–3 ml. of concentrated sulphuric acid. 0.1N-Ceric sulphate solution was run in slowly from a burette with continuous agitation to approximately 1 ml. from the end-point. [A rough end-point was obtained on noting the yellow colour of excess of cerium(IV) ions in the absence of indicator.] 5 Drops of the orthanilic acid solution, or 1 drop of the benzidine-3,3'-disulphonic acid solution, were now added, and the ceric sulphate solution was added dropwise until the bright yellow colour of the end-point was reached.

Electrophoretic Studies.—The solutions for examination were prepared by oxidising 5 ml. of 0.5% aqueous anthranilic or orthanilic acid containing 2 ml. of 4M-sulphuric acid with 1.5 ml. of 0.1N-cerium(IV) sulphate, then immediately reducing with 1.5 ml. of 0.1N-iron(II) sulphate. The solution derived from anthranilic acid was treated on a column of Zeo-Karb 225 to remove sulphate ions; the amino-acids were adsorbed on the resin and eluted with N-ammonia solution. The eluate was concentrated under reduced pressure, portions of the solution were transferred to Whatman No. 3 paper, and electrophoresis was carried out for 2 hr. in a borate buffer (pH 10) at 1000v, conventional equipment being used.⁸ The paper was then dried and sprayed with cerium(IV) sulphate solution. Anthranilic acid produced a pink spot, and benzidine-3,3'-dicarboxylic acid, with a slightly lower migration rate, a yellow spot.

The solution derived from orthanilic acid was similarly treated, but because the amino-acids were not adsorbed on the cationic resin, the eluate was treated with Deacidite F to remove sulphate ions. After electrophoresis, orthanilic acid gave a pink spot on the paper with cerium(IV); benzidine-3,3'-disulphonic acid, with a slightly greater migration rate, gave a yellow spot.

Polarographic Studies.—The Electrochemical Laboratories manual (Model BMK) polarograph together with the Pye Scalamp galvanometer were used. A 0.0005M-solution of anthranilic acid in 0.5M-sulphuric acid solution was subjected to a steadily increasing voltage applied between a dropping-mercury anode and a saturated calomel electrode as cathode in the usual way.

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⁷ Belcher, Nutten, and Stephen, *J.*, 1952, 3857.

⁸ Linstead, Elvidge, and Whalley, "A Course in Modern Techniques of Organic Chemistry," Butterworths, London, 1955.

⁹ Syrokonskii and Stiepin, *J. Amer. Chem. Soc.*, 1936, 58, 928.

¹⁰ Belcher, Rees, and Stephen, *Chim. analyt.*, 1959, 41, 397.

¹¹ Belcher, Lyle, and Stephen, *J.*, 1959, 4454.

¹² Kolthoff and Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers Ltd., 1957.