470. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XIV.* 3-Bromo- and 3 : 3′-Dibromobenzidine as Redox Indicators.*

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3-Bromo- and 3 : 3-dibromo-benzidine undergo reversible oxidation in inorganic redox systems. These compounds can be used as redox indicators in the titration of iron(II) with potassium dichromate and with ceric sulphate. Sharp end-points (colourless to yellow) are obtained.

IT has been suggested that, in the benzidine series, meriquinonoid salts stable to further and irreversible oxidation could probably only be obtained by *N*-alkylation.[1] Although the properties of nuclear alkyl-substituted benzidines do not differ greatly from those of the parent diamine [2] we now find that substitution by chlorine or bromine in the 3- and 3 : 3′-positions (but not in the 2- or 2 : 2′-positions) gives products with many oxidising agents which are highly coloured and more stable than those given by the parent diamine. The present study describes the behaviour of these four halogenated benzidines in conventional inorganic redox systems, and an assessment of their value as redox indicators.

All four compounds undergo the reactions characteristic of benzidine. In dilute acetic acid, the colours vary from blue-green for the monosubstituted to green for the disubstituted compounds, all changing to bright yellow or orange-yellow on the addition of dilute mineral acid. Similar yellow products are obtained by direct oxidation of the compounds in dilute mineral acid; the only difference observed is that the bromo-derivatives give a more orange-yellow colour than the chloro-derivatives which are oxidised to bright canary-yellow products. The colours which appear in dilute acetic acid are not very stable and fade in 10—15 minutes, but those formed in mineral acid only gradually decrease in intensity.

The oxidation of these halogenated benzidines in aqueous solutions is reversible. With the majority of simple benzidine derivatives, this process is too slow to allow of their use as indicators in redox titrimetry; only one such compound, *o*-dianisidine (3 : 3′-dimethoxybenzidine), has been used to any extent as a redox indicator. The halogenated benzidines, however, showed a sufficiently sharp colour change in solution to warrant their application for this purpose. When they were used in the titration of iron(II) with potassium dichromate and ceric sulphate all four behaved reversibly, but only 3-bromo- and 3 : 3′-dibromo-benzidine gave sharp enough end-points to have practical applications. 3-Chloro- and 3 : 3′-dichloro-benzidine reacted sluggishly and although end-points could be detected quite readily the titrant had to be added very slowly in the region of the end-point to allow time for the indicator reaction. The bromo-derivatives on the other hand responded instantly to the addition of either the oxidant or the reductant, and the colour change at the end-point could be obtained many times without apparent destruction of the organic compounds. At elevated temperatures, the indicator reaction still occurs, but is accompanied by some destruction of the reversibly formed oxidation products.

The transition potentials of 3-bromo- and 3 : 3′-dibromo-benzidine have been determined, the apparatus and procedure described previously [3] being used, and the results for each indicator over a range of acid concentrations are tabulated. These potentials lie midway between the accepted values for diphenylamine-4-sulphonic acid and tris-(1 : 10-phenanthroline) ferrous sulphate (840 and 1080 mv, respectively in M-sulphuric acid). Potentiometric studies of the ferrous–dichromate and ferrous–ceric titrations show that

* Part XIII, *J.*, 1954, 2543.

[1] Belcher, Nutten, and Stephen, *J.*, 1954, 2543.

[2] Belcher and Nutten, *J.*, 1951, 546.

[3] *Idem, J.*, 1952, 3857.

both bromobenzidine indicators function in the potential range over which the end-points of these titrations occur.

Transition potentials (mv, *referred to the hydrogen electrode*) *of* 3-*bromo- and* 3 : 3′-*dibromo-benzidine in various concentrations of sulphuric acid at* 18°.

	3-Bromobenzidine					*3 : 3′-Dibromobenzidine*				
Acid concn. (M) ...	0·5	1·0	2·0	4·0	8·0	0·5	1·0	2·0	4·0	8·0
E.M.F. (mv)	892	900	912	920	—	920	936	954	960	965

No simple benzidine derivative has been found which has a transition potential as high as those of the bromo-derivatives. Only one other substance, *N*-phenylanthranilic acid (diphenylamine-2-carboxylic acid) which depends on coloured meriquinonoid oxidation products for its use as a redox indicator, is reported [4] as having a similarly high transition potential (1080 mv) (our preliminary observations on this indicator point to a transition potential much nearer to that of the bromobenzidines).

In titrations of iron(II) solutions with both potassium dichromate and ceric sulphate, the dibromo-derivative gives the sharper end-point, this difference becoming more noticeable as the acidity of the solution is increased above the optimum acidity of 2M for both indicators. In the iron(II)–dichromate titration, it is unnecessary to add phosphoric acid. Titrations in hydrochloric acid are unsatisfactory because at the end-point the yellow colour of the ferric chloride obscures the colours of the oxidised indicators.

Both indicators function well in solutions warmed to 60°, which suggested their use in the direct titration of oxalic acid with ceric sulphate. It was found, however, that the indicators themselves were oxidised beyond the meriquinonoid stage, even when they were added near the equivalence point of the titration. Satisfactory end-points were only obtained in the presence of large amounts of indicator which, in turn, gave rise to high results for the titration.

Results for the titration of iron(II) with 0·1N-ceric sulphate and 0·1N-potassium dichromate showed good agreement (±0·02%) between the experimental and the theoretical titres.

Methods for the preparation of 3 : 3′-dichloro- and 3 : 3′-dibromo-benzidine are reported in the literature. Cohn [5] obtained 3 : 3′-dichlorobenzidine by the reduction of *o*-chloronitrobenzene with zinc dust and alkali; Synder, Weaver and Marshall [6] used a similar reaction for the preparation of 3 : 3′-dibromobenzidine. We prefer to use the procedure described by the latter workers for the preparation of the dichloro-derivative also. Only a procedure involving the condensation of *o*-chloro- or *o*-bromo-aniline with nitrosobenzene proved satisfactory for the preparation of the appropriate azo-compound leading to 3-chloro- or 3-bromo-benzidine. Bamberger [7] mentioned this reaction for the preparation of 3-chloro- and 3-bromo-azobenzene, but he gave no experimental details. 2-Chloro- and 2-bromo-azobenzene so obtained were reduced with zinc dust and alkali, and the hydrazo-compounds then rearranged to the required benzidines.

EXPERIMENTAL

Determination of the Transition Potentials of 3-*Bromo- and* 3 : 3′-*Dibromo-benzidine*.—The previously described [3] apparatus and procedure were used.

Solutions required: [3] Potassium dichromate, 0·1N. Ceric sulphate, 0·1N. Ferrous ammonium sulphate, 0·1N. Sulphuric acid, 2M.

Indicator solutions. 3-Bromo- or 3 : 3′-dibromo-benzidine (0·2 g.) was dissolved in warm glacial acetic acid (100 ml.).

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[4] Syrokomsky and Stiepin, *J. Amer. Chem. Soc.*, 1936, **58**, 928.

[5] Cohn, *Ber.*, 1900, **33**, 3552.

[6] Snyder, Weaver, and Marshall, *J. Amer. Chem. Soc.*, 1949, **71**, 289.

[7] Bamberger, *Ber.*, 1900, **33**, 3190.

Titration of Iron(II).—The iron(II) solution (5—25 ml.) was diluted to 100 ml. with 2M-sulphuric acid, and four drops of indicator were added. Potassium dichromate was run in from a burette, rapidly at first, then more slowly as the end-point was approached. The addition of dichromate was continued dropwise with shaking until a permanent colour change to yellow was obtained.

The same procedure was followed with ceric sulphate as the titrant.

Preparation of the Amines.—3 : 3′-*Dichlorobenzidine.* The procedure of Snyder, Weaver, and Marshall was followed, with the appropriate amount of *o*-chloronitrobenzene in place of *o*-bromonitrobenzene. The yield of 3 : 3′-dichlorobenzidine dihydrochloride was 40%. The free base, recrystallised from light petroleum (b. p. 60—80°), had m. p. 133°.

3-*Chlorobenzidine.* To nitrosobenzene (10·5 g.) in glacial acetic acid (30 ml.), *o*-chloroaniline (15 g.) in the same solvent (20 ml.) was added. The mixture was left overnight, then poured into *ca.* 1 l. of water. Alkali was added until the solution was almost neutralised, the remaining acid being removed with sodium carbonate. The mixture was extracted with ether, and the ethereal solution treated with ethereal hydrogen chloride. The precipitate of *o*-chloroaniline hydrochloride was filtered off, and the filtrate evaporated to about 100 ml. This solution containing 2-chloroazobenzene was subjected to column chromatography on alumina, the azo-compound being eluted with ether. The eluate was evaporated and the remaining red oil was cooled in ethanol–solid carbon dioxide. The crystalline mass was allowed to warm to 0° and the crystals were rapidly filtered off. This process of cooling, warming, and filtering was repeated with the oily residues until most of the azo-compound was obtained crystalline. The 2-*chloroazobenzene* (45%) had m. p. 33° (Found: C, 66·6; H, 4·0; N, 12·9; Cl, 16·6. $C_{12}H_9N_2Cl$ requires C, 66·5; H, 4·2; N, 13·0; Cl, 16·4%).

2-Chloroazobenzene (5·5 g.) was dissolved in ethanol (50 ml.), and zinc dust (3·5 g.) was stirred into the mixture. A solution of sodium hydroxide (4 g. in a few ml. of water, made up to 50 ml. with ethanol) was added, the whole was boiled under reflux until the red colour had disappeared (after about 45 min.), then filtered into an excess of concentrated hydrochloric acid, and the residue of zinc oxide was washed with warm ethanol, the washings being added to the main bulk of filtrate. 3-Chlorobenzidine hydrochloride was precipitated from the filtrate and was recrystallised from dilute hydrochloric acid (yield, 5 g., 66%). The free *base* recrystallised from light petroleum (b. p. 40—60°) as needles, m. p. 75° (Found: C, 66·1; H, 5·2; N, 12·8; Cl, 16·1. $C_{12}H_{11}N_2Cl$ requires C, 65·9; H, 5·1; N, 12·8; Cl, 16·2%).

3-*Bromobenzidine.* The same procedure was followed, with 20 g. of *o*-bromoaniline in place of *o*-chloroaniline. 2-*Bromoazobenzene* was obtained as red crystals, m. p. 36° (30%) (Found: N, 10·7; Br, 30·5. $C_{10}H_9N_2Br$ requires N, 10·7; Br, 30·6%). This (7·5 g.) was reduced as was the 2-chloro-compound (2 hours' reflux). 3-Bromobenzidine dihydrochloride was obtained in 50% yield. The *base* recrystallised from light petroleum (b. p. 40—60°) as needles, m. p. 81° (Found: N, 10·5; Br, 32·7. $C_{10}H_{11}N_2Br$ requires N, 10·7; Br, 32·9%).

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