Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XIII. The Behaviour of Certain* N- *and* NN′-*Alkylated Benzidines towards Oxidising Agents.*

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N-Methyl-, *NN*′-dimethyl-, and *NN*′-tetramethyl-benzidine and the corresponding ethyl derivatives have been examined as colorimetric reagents for oxidising agents. These compounds are more sensitive towards oxidising agents than are the simple diamines; the products of their oxidation are exceptionally stable. Their applicability as redox indicators is also discussed.

Benzidine has been widely used for the colorimetric determination of various oxidising agents, but suffers from the disadvantage that its coloured oxidised form is very unstable and the colour fades rapidly. In an earlier paper of this series, Belcher and Nutten (*J.*, 1951, 546) examined the reactions of several nuclear-substituted benzidines with oxidising agents and showed these to be more satisfactory reagents than benzidine. Little work has, however, been reported on the analytical applications of the *N*- and *NN*′-substituted benzidines, although Hovorka (*Coll. Czech. Chem. Comm.*, 1948, **13**, 520) has described the uses in analytical chemistry of several *NN*′-dialdobenzidines, and of *NN*′-diacetyl-, *NN*′-dibenzoyl-, and *N*-monovanillylidene-benzidine. *NN*′-Diphenylbenzidine, the immediate oxidation product of diphenylamine, has found several applications in colorimetry and is used extensively as a redox indicator.

We have now examined several mono-, di-, and tetra-*N*-alkylbenzidines in order to assess their applicability as analytical reagents and particularly to study their behaviour towards oxidising agents. In connection with their studies on the mechanism of the oxidation of Alphazurine-G, Adams and Hammaker (*Analyt. Chem.*, 1951, **23**, 744) examined the indicator properties of *NN*′-tetramethylbenzidine and its 3-sulphonic acid. Their findings and ours are compared below.

Reactions with Oxidising Agents.—All the *N*- and *NN*′-alkylbenzidines used gave highly coloured products with many oxidising agents. In dilute acetic acid, the colours obtained were greenish-blue for the monoalkyl-, greenish-yellow for the dialkyl-, and bright yellow for the tetra-alkyl-benzidines. The colours of the ethyl derivatives were generally less intense. In mineral acid, all the amines gave bright yellow oxidation products.

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* Part XII, *J.*, 1953, 1334.

The sensitivities of the amines towards oxidising agents in both acetic acid and mineral acid solution were determined. The results for selected oxidising agents are given in the Tables below, with those for benzidine included for comparison.

Ion sensitivities (µg. per ml.): acetic acid solution.

Benzidine	MnO_4^{1-}	$Cr_2O_7^{2-}$	VO_3^{1-}	Fe^{3+}	$S_2O_8^{2-}$	IO_4^{1-}	ClO^{1-}	$Fe(CN)_6^{3-}$	Ref. to preptn
(Unsubst.)	0·3	4	5	—	5	8	0·7	2	
N-Me	0·1	0·5	1	0·8	2	2	0·1	0·5	1
NN'-Me_2	0·05	0·25	0·25	0·4	0·5	0·7	0·1	0·4	2
NN'-Me_4	0·1	0·5	0·5	0·5	0·6	1	0·3	0·3	3
N-Et	0·1	0·8	1	1	2	2	0·2	0·5	4
NN'-Et_2...	0·1	1	0·8	0·8	25	5	0·2	0·4-	5
NN'-Et_4...	0·1	2	0·8	7	2	8	0·5	0·5	6

1, Rassow, *J. pr. Chem.*, 1911, **84**, 273. 2, Willstätter and Kalb, *Ber.*, 1904, **37**, 3773. 3, Ullmann and Dieterle, *ibid.*, p. 23. 4, Rassow, *loc. cit.*, p. 349. 5, Bamberger and Tichvinsky, *Ber.*, 1902, **35**, 4190. 6, Ullmann and Dieterle, *loc. cit.*, p. 33.

Ion sensitivities (µg. per ml.): hydrochloric acid solution.

Benzidine	$Cr_2O_7^{2-}$	VO_3^{1-}	IO_3^{1-}	BrO_3^{1-}	IO_4^{1-}	$S_2O_8^{2-}$	Cl_2
(Unsubst.)	5	5	1	—	20	20	1
N-Me	1	1·5	0·2	4	3	1	0·5
NN'-Me_2	0·4	0·4	0·1	5	1	0·4	0·25
NN'-Me_4	0·6	0·6	0·1	4	1	0·7	0·2
N-Et	0·5	0·5	0·25	5	2	0·5	0·5
NN'-Et_2	2	1·5	0·1	5	2	10	0·25
NN'-Et_4	2	2	—	—	—	2	0·5

All the *N*- and *NN'*-alkylbenzidines examined are more sensitive than benzidine towards oxidising agents. In acetic acid solution, the sensitivities of the *N*-methyl derivatives tend to be greater than those of the corresponding *N*-ethyl compounds. Moreover, the oxidation colours of all these amines are very stable. Of the amines described, two in particular, *NN'*-dimethyl- and *NN'*-tetramethyl-benzidine, should prove useful reagents for the detection and perhaps determination of oxidising agents. They are superior in every respect to the simple diamines which generally provide only transient colours with many oxidising agents. The secondary and tertiary amino-groups do not prevent the formation of the coloured product, but they do appear to inhibit the further oxidation of the molecule.

If this be so, the secondary and tertiary bases derived from numerous diamines of the benzidine series should be of much greater value as colorimetric reagents than the diamines themselves. In this investigation only the *N*- and *NN'*-alkylated benzidines have been studied; it would be interesting to examine several *N*- and *NN'*-alkylated 2 : 7-diaminophenylene oxides or 2 : 7-diaminofluorenes since both simple diamines give colour reactions which are much more sensitive than those given by benzidine but very transient.

Applications as Redox Indicators.—Adams and Hammaker (*loc. cit.*) have recommended *NN'*-tetramethylbenzidine and its 3-sulphonic acid as indicators for the titration of ferrous solutions with ceric sulphate. In the present work, none of the indicators proved to be of use in ferrous–ceric sulphate titrations, as the slow development of colour gave sluggish end-points with over-consumption of reagent. The oxidised form of *NN'*-tetramethylbenzidine was remarkably stable at high temperatures and this suggested its application as an indicator in oxalate–ceric sulphate titrations, but again the end-points were sluggish.

The applications of these alkylated benzidines appear to lie, not in titrations using ceric sulphate or potassium dichromate as oxidants (for which satisfactory indicators are generally available), but in replacement of benzidine; *e.g.*, *NN'*-dimethyl- or *NN'*-tetramethylbenzidine should be satisfactory in the titration of gold with quinol, silver with bromide or iodide, or vanadate with ferrous iron. Belcher and Nutten (*J.*, 1951, 547, 548) found that, in these titrations, nuclear-substituted benzidines gave considerably improved end-points.

Preparation of Amines.—Methods for the preparation of all these alkylated benzidines are described in the literature and with one exception they proved satisfactory: *N*-ethylbenzidine could not be obtained by the method of Rassow (*loc. cit.*), who obtained only a negligible yield (*ca.* 1%); Gilman *et al.* (*J. Amer. Chem. Soc.*, 1945, **67**, 922) prepared this compound by reaction of diethylbarium with azobenzene and rearrangement of the substituted hydrazobenzene with acid. Both these preparations were unsuitable for our purposes and an alternative synthesis was evolved. 4-Amino-4′-nitrodiphenyl, dissolved in acetone, was heated in a sealed tube with ethyl iodide, affording 4-ethylamino-4′-nitrodiphenyl; on reduction with zinc dust and hydrochloric acid, 4-amino-4′-ethylaminodiphenyl (*N*-ethylbenzidine) was obtained.

EXPERIMENTAL

(I) *Sensitivity Determinations.—Solutions required. Amine reagents.* 1% Solutions of each base in 5% acetic acid and in 1N-hydrochloric acid.

Procedure. (i) Acetic acid solution. One drop of amine reagent in acetic acid was added to 1 ml. of the neutral test solution contained in a micro-test tube and the colour formed was viewed against a white background. The procedure was repeated with more dilute solutions of the oxidising ions until a change of colour was just observed after 30 sec.

(ii) Hydrochloric acid solution. The above procedure was repeated but with the amine reagents in hydrochloric acid.

(II) *Applications as Redox Indicators.—Solutions required. Indicator solutions.* 1 g. of each base was dissolved in 100 ml. of 1N-sulphuric acid.

Ceric sulphate. 0·1N (*J.*, 1952, 1273).

Titration of ferrous iron. 0·1N-Ferrous ammonium sulphate solution (see *J.*, 1952, 1273) was acidified with sulphuric acid, 4 drops of indicator were added, and the solution was titrated with 0·1N-ceric sulphate solution (*ibid.*). Titrations were also carried out in the presence of phosphoric acid.

(III) *Preparation of* N-*Ethylbenzidine.*—4-Amino-4′-nitrodiphenyl (8 g.) (for preparation, see *J.*, 1953, 1336) was dissolved in acetone (50 ml.), and ethyl iodide (15 g.) added. The mixture was sealed in a glass tube and warmed for 3 hr. in a boiling-water bath. The tube was cooled and opened, and the contents were poured into water. Ethyl iodide and acetone were removed by distillation, and the residue was made alkaline and filtered. The orange-red solid was washed well with water, drained, and oven-dried (80°). It was recrystallised from acetone, forming large, orange-red, glistening plates (5 g.), m. p. 168°.

This amine (5 g.) was suspended in ethanol (50 ml.), concentrated hydrochloric acid (10 ml.) was added, and the mixture was boiled under reflux. Zinc dust (12 g.) was added in small portions to the boiling solution (15 min.), and the almost colourless solution was refluxed for a further 30 min. The ethanol was distilled off, and the residue made alkaline. The liberated base was extracted with ether, the ether evaporated off, and the remaining semi-solid material recrystallised from methanol. The base formed very pale yellow prisms (3 g.), m. p. 85°. The hydrochloride and sulphate were isolated only with difficulty.

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