115. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part II. Reaction with Oxidising Agents.*

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The sensitivities of the substituted benzidines and related compounds described in the first paper of this series towards various oxidising agents have been determined. Several amines were found to be more sensitive in their reaction than benzidine.

BENZIDINE is easily oxidised to a blue meriquinonoid compound containing one molecule of a *p*-quinonoidal oxidation product and one molecule of the base (Schlenk, *Annalen*, 1908, **363**, 313). Many applications have been found for this reaction in analytical chemistry and very sensitive tests are available for ions containing molybdenum, phosphorus, chromium, manganese, cerium, lead, and gold.

It has been claimed that two of the amines described in Part I (preceding paper) are more sensitive than benzidine in their reactions with certain oxidants. 2 : 7-Diaminofluorene is 10 times more sensitive towards persulphate than is benzidine (Schmidt and Hinderer, *Ber.*, 1932, **65**, 89), and 2 : 7-diaminodiphenylene oxide can be used with advantage in place of benzidine for the detection of ions with oxidising properties (Cullinane and Chard, *Analyst*, 1948, **73**, 95). The results of the latter workers may be summarised here, because the conditions obtaining during their sensitivity tests differ to a large extent from those employed by us. The reagents used were 0·75% solutions of benzidine and 2 : 7-diaminodiphenylene oxide in 10% (v/v) glacial acetic acid. A drop of reagent was added to a drop of neutral ion test solution, and the colour produced observed. Results given by various oxidising ions are listed in Table I. The limits of identification refer to 1 drop of test solution.

TABLE I.

Ion.	Limit of identification (μg.). Benzidine.	2 : 7-Diaminodiphenylene oxide.	Ion.	Limit of identification (μg.). Benzidine.	2 : 7-Diaminodiphenylene oxide.
Ag^{1+}	6·35	0·64	CrO_4^{2-}	0·27	0·003
Fe^{3+}	0·12	0·06	$Fe(CN)_6^{3-}$	1	0·1
Pt^{6+}	12·5	0·13	IO_4^{1-}	0·5	0·23
Au^{3+}	1	1	$S_2O_8^{2-}$	0·1	0·01
Tl^{3+}	0·04	0·04	VO_3^{2-}	1·8	0·05
Ce^{4+}	0·18	0·09	BiO_3^{1-}	0·15	0·15

No other reference to the oxidation reaction sensitivities of substituted benzidines and related compounds could be found; accordingly, the sensitivities of these compounds towards certain oxidising agents have been determined. Only those sensitivities which might be applicable in analytical chemistry are listed; for instance, naphthidine will give a direct red colour with most oxidising agents, but the reactions are not sufficiently sensitive to warrant its use for their detection.

Benzidines with substituents in the 2-position cannot be oxidised to a blue meriquinonoid compound.

The behaviour of the series of amines towards the following common cations and anions was also studied :

Ag^{1+}, Hg^{1+}, Hg^{2+}, Pb^{2+}, Cu^{1+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Be^{2+}, Ti^{3+}, Ti^{4+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Zr^{4+}, Sn^{2+}, Sn^{4+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}, NH_4^{1+}, Na^{1+}, Li^{1+}, Tl^{1+}, Tl^{3+}, K^{1+}, UO_2^{2+}.

PO_4^{3-}, CN^{1-}, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, F^{1-}, Cl^{1-}, Br^{1-}, I^{1-}, ClO_4^{1-}, CNS^{1-}, NO_3^{1-}, AsO_3^{3-}, AsO_4^{3-}, SbO_3^{3-}, SbO_4^{3-}, WO_4^{2-}, MoO_4^{2-}, SeO_4^{2-}, SeO_3^{2-}, TeO_4^{2-}, TeO_3^{2-}.

Certain of the amines slowly yielded precipitates with WO_4^{2-} in N-hydrochloric acid. The quantitative aspects of these reactions are being investigated and will be reported later.

The complexes which these amines form with metallic salts were not examined as they have no suitable applications in modern analytical chemistry.

The sensitivities of the amines towards oxidising agents in neutral solution were determined, with the results shown, in Table II(*a*); blue-green products were obtained except from 4-aminodiphenylamine, which gave a violet colour.

TABLE II.

Ion sensitivity, μg./ml.

	(*a*) In neutral solution.							(*b*) In acid solution.		
Amine.	MnO_4^{1-}.	$Cr_2O_7^{2-}$.	CrO_4^{3-}.	VO_3^{2-}.	$S_2O_8^{2-}$.	IO_4^{1-}.	Fe^{3+}.	VO_3^{2-}.	IO_3^{1-}.	BrO_3^{1-}.
Benzidine	0·5	5	10	10	10	40	10	10	1	—
3-Methylbenzidine	0·5	3	8	9	10	50	8	7	1	30
3 : 3′-Diethylbenzidine	0·7	4	8	10	10	60	10	10	1	30
2 : 7-Diaminofluorene	0·5	0·6	1	2	1	2	2	3	5	—
N-Methylbenzidine ...	0·75	7	10	100	3	80	10	10	1	—
4-Aminodiphenylamine	—	10	4	8	20	8	8	—	4	—

In acid solution a yellow oxidation product was formed, but again that from 4-aminodiphenylamine was violet. With the vanadate ion a more sensitive test was obtained with certain amines. Iodate and bromate ions gave this yellow colour in acid solution though they did not oxidise the amines in neutral solution. Sensitivities obtained under acid conditions are included in Table II(*b*).

Experimental.—(1) 1 Ml. of neutral ion test solution was measured into a micro-test tube, and 1 ml. of a 0·25% solution of the amine hydrochloride added. The contents of the tube were shaken and the colour formed was viewed against a white background. The ion solution was then diluted, and the procedure repeated until no colour could be detected within 30 seconds.

(2) 1 Ml. of the ion test solution in 0·1N-hydrochloric acid was treated as above with 1 ml. of amine hydrochloride solution, and the colour sensitivites determined.

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