SPECTROPHOTOMETRIC DETERMINATION OF SOME ORGANIC NITROGEN BASES AND IODINE IN DICHLOROETHANE

U. MURALIKRISHNA, N. SOMESWARA RAO AND G. V. RAMANADHAM

Department of Chemistry, Andhra University, Waltair

ABSTRACT

A new, rapid and simple spectrophotometric method for the determination of brucine, strychnine, 1, 10 phenanthroline, 2, 2′ bipyridyl and iodine has been developed based on the formation of triiodide ion *via* the charge transfer complex formation. Dichloroethane is found to be the most suitable solvent.

INTRODUCTION

SPECTROPHOTOMETRIC determination of a number of compounds (donors and acceptors forming charge transfer complexes) is based on the charge transfer band maxima of the complexes[1-4]. Some methods reported for the estimation of the bases are generally based on their basic[5,8] and redox[5-7], properties and on spectral characteristics[9] of these donors.

Brucine and strychnine have been estimated titrimetrically[5] involving the formation of relatively insoluble compounds with bichromate, mercury (II) and thiocyanate, the method being completed by titrating the excess reagent suitably. These procedures obviously are time consuming ; 1, 10-phenanthroline and 2, 2′-bipyridyl are determined[5] anologously, based on the formation of the insoluble silver(II) salts. The titrimetric[10] determination of 1, 10-phenanthroline, 2, 2′-bipyridyl, brucine and strychnine in 50% acetic acid-acetic anhydride solvent, potentiometrically with perchloric acid, indicates that these are monoacidic bases.

We have earlier reported[11] a spot test for the detection of 1, 10-phenanthroline, iodine and iodate, based on the formation of a complex between the base and iodine. However, there seems to have been no report of the determination of these nitrogen bases, utilizing the ultimate formation of triiodide ion. The present paper describes the spectrophotometric determination of these bases with iodine *via* the inner complex formation. Incidentally it is possible to utilize the procedure for the determination of iodine also. The method is quite simple and rapid as compared to earlier methods.

EXPERIMENTAL

Reagents.—1, 10-phenanthroline (E. Merck)) was dried at 105° C and recrystallised from benzene. (m.p. 117° C). 2, 2′-Bipyridyl (E. Merck) was recrystallised from benzene. Iodine (B.D.H. India A.R.) was purified by resublimation under reduced pressure. Chloroform, 1, 2-dichloroethane. methanol were used after purification by distillation by standard methods[12]. Brucine and strychnine

(chempure, Analar) were recrystallised from chloroform.

PROCEDURE

Spectra.—Absorption measurements were made with Beckmann D U Spectrophotometer at room temperature (25° C) using matched silica cells, 1 cm pathlength. The spectra of the mixtures of brucine-iodine, 1, 10-phenanthroline-iodine, 2, 2′-bipyridyl-iodine, strychnine-iodine in the solvent were scanned with iodine in the solvent as blank. A characteristic new band at about 365 nm indicates the formation of triiodide ion, *i.e.*, inner complex formation. The colour of the solution at this stage is yellow.

Procedure for the nitrogen bases.—Suitable aliquots of the nitrogen bases from the stock solutions, prepared by dissolving accurately weighed samples in the solvent, are transferred to 10 ml volumetric flask. Iodine solution (1 ml) is added to each flask and the contents made up to the mark with the solvent. The absorbance of the solutions are measured at the 365 nm against the reagent blank. A calibration curve is drawn from the results. The sample solution is then treated with an excess of the reagent and its absorbance measured against the reagent blank. The amount of the base is then read off from the calibration curve.

TABLE I
Titrimetric determination of mole ratio

Volume of 1,10-phenan-throline (O.P.)	Volume of iodine	Amount of O.P. (gm)	Amount of iodine (gm)	Mole ratio I_2/O.P.
10 ml.	7·8 ml.	0·2507	0·4705	1·866
10 ml.	8·1 ml.	0·2507	0·4887	1·938
10 ml.	3·1 ml.	0·2493	0·5260	2·087
10 ml.	3·2 ml.	0·2493	0·5420	2·155

Procedure for iodine.—Suitable aliquots of iodine from the stock solutions, prepared by dissolving weighed samples in chloroform are transferred to

TABLE II
Spectrophotometric determination of nitrogen bases and iodine

Solvent	Reagent	Constituent determined	Amount of constituent (μg/ml)	
			Taken	Found
Chloroform	Brucine	Iodine	2·00	2·00
			5·00	5·02
			10·00	9·95
			20·00	19·90
Chloroform	Iodine	Strychnine	5·00	5·00
			10·00	10·10
			20·00	19·95
			30·00	29·50
Chloroform	Iodine	Brucine	0·60	0·60
			1·50	1·51
			3·00	2·98
			6·00	5·98
			15·00	14·95
Chloroform	Strychnine	Iodine	10·00	10·00
			20·00	20·20
			40·00	39·50
1, 2, Dichloroethane	Iodine	Brucine	0·40	0·40
			0·80	0·805
			2·40	2·42
			3·60	3·55
1, 2, Dichloroethane	Brucine	Iodine	0·90	0·90
			2·60	2·62
			8·50	8·40
			22·00	21·55
1, 2, Dichloroethane	Iodine	1, 10-phenanthroline	155	156
			225	223
			340	344
			455	449
1, 2, Dichloroethane	Iodine	2, 2′ Bipyridyl	320	322
			450	455
			578	572
			650	645
1, 2, Dichloroethane	Iodine	Strychnine	2·00	2·00
			4·50	4·45
			12·00	11·90
			18·50	18·40
Methanol	Iodine	Strychnine	9·50	9·80
			2·40	2·55
			10·50	10·80
			20·00	20·50
Methanol	Iodine	Brucine	1·50	1·60
			3·00	3·10
			9·50	9·80
Methanol	Iodine	1, 10-phenanthroline	60·0	61·5
			90·0	92·5
			125·0	120·0
			215·0	220·0
Methanol	Iodine	2, 2′ Bipyridyl	120·0	124·0
			224·0	229·0
			340·0	348·0
			450·0	460·0

10 ml volumetric flasks. One millilitre of brucine solution (excess) is added to each flask and the contents made up to the mark with the solvent. The absorbance of the solutions are measured at 365 nm against the reagent blank. The concentration of the unknown solution is calculated by referring the absorbance data to the calibration curve.

RESULTS AND DISCUSSION

In our previous communication[11], we have reported the formation of a blue precipitate which slowly changes its colour to brown in course of time. Further it has also been observed that the absorbance of a solution of 1, 10–phenanthroline and iodine in chloroform at 365 nm increases. This is probably due to the transformation of an outer complex to inner complex.

Ashworth *et al.*[13] studied the polarovoltric end point method for the titration of organic nitrogen bases, with iodine. They also found that some precipitate first forms which then takes on some more iodine to form an iodine richer product but could not explain the widely fluctuating data. The gravimetric method, as also the titrimetric method (of back titrating the excess iodine in the filtrate) in this investigation showed that the stoichiometry of 1, 10–phenanthroline : iodine = 1 : 2 (approx.) as can be seen from the results in Table I. Our results on the gravimetric and titrimetric methods are exactly similar to those of Ashworth *et al.*[13].

However, such difficulties in the spectrophotometric determination of these bases do not seem to arise with 1, 2-dichloroethane as the solvent (Table II). The deviations observed in the gravimetric or titrimetric method may be due to slow transformation of the outer complexes, first formed to inner complexes. With comparatively stronger bases like brucine and strychnine the formation of the inner-complex and consequently the trihalide ion may be fast enough, so that the determination of these bases by the spectrophotometric method is not beset with such discrepancies. Similar type of fast transformations with the consequent immediate triiodide ion formation in more polar solvents has been reported earlier[14-17].

The deviations observed in chloroform in the case of 1, 10–phenanthroline and 2, 2'–bipyridyl also can be explained as due to the dependence of the transformation of the outer complex to inner complex and the dielectric constant. The variation to the extent of 5%, in the determination of these bases in methanol, may be due to the probable photo dissociation[18 19] of iodine-methanol complex.

1. Bauer, R. H., *Anal. Chem.*, 1963, 35, 107.
2. Schenk, G. H., *Ibid.*, 1965, 37, 372.
3. Sharma, J. P. and Tiwari, R. D., *Micro. Chem. J.*, 1972, 17, 151.
4. — and —, *Micro. Chim. Acta (Wien)*, 1974, p. 323.
5. Ash Worth, M. R. F., *Titrimetric Organic Analysis*, Vol. II, Interscience Publishers, New York, London, 1965.
6. Vestfal, N. I., *Aptechnoe delo*, 1958, 7 (3), 27.
7. Karmazin, M. and Bosward, J., *Pharm. Zentralhave*, 1956, 95, 10.
8. Gautier, J. A., Renault, J. and Rabiant, J., *Ann. Pharm. France*, 1959, 17, 401.
9 El Ridi, M. S. and Khalifa, K., *Proc. Pharm Soc. Egypt. Sci. Ed.*, 1953, 35 (77), 31.
10. Tun Tao, and Hsing-Yun yu, *Yao Hsuesh Hsueh pao*, 1960, 8, 206.
11. Muralikrishna, U. and Someswararao, N., *Curr. Sci.* (Communicated).
12. Weissberger, A., *Technique of Organic Chemistry*, Vol. VII, Interscience, New York, 1955.
13. Ashworth, M. R. F. and Hartmann. U., *Anal. Chim. Acta*, 1967, 38, 415.
14. Reid, C. and Mulliken, R. S., *J. Am. Chem. Soc.*, 1954, 76, 3869.
15. Mulliken, R. S., *J. Phys. Chem.*, 1952, 56, 801.
16. Bhat, S. N. and Rao, C. N. R., *J. Am. Chem. Soc.*, 1966, 88, 3216.
17. Bhaskar, K R., Bhat, S. N., Singh, S. and Rao, C. N. R., *J. Inorg. Nucl. Chem.*, 1966, 28, 1915.
18. Kimura, K., Achiba, Y. and Katsumata, S., *J. Phys. Chem.*, 1973, 77, 2520.
19. Fornier, de Voilet, P., Bonneau, R. and Joussot-Dubien, J., *Chem. Phys. Lett.*, 1973, 19, 251.