

CI.—*The Colour and Constitution of the Alkyl Iodides of Cyclic Bases.*

By CHARLES KENNETH TINKLER.

It has previously been observed by various investigators that in a large number of cases the alkyl iodides of cyclic bases are coloured substances, the alkyl bromides slightly coloured, whilst the corresponding alkyl chlorides, hydrochlorides, and oxygen salts are colourless. In addition, it has been noticed that whilst these alkyl iodides give strongly-coloured solutions in chloroform, dilute aqueous or alcoholic solutions are colourless. In the case of the acridines, where the hydrochlorides and oxygen salts are themselves coloured, the solutions of the alkyl iodides in water and alcohol are similarly coloured, whilst the chloroform solutions are much darker in colour.

Decker (*Ber.*, 1904, **37**, 2938) explained the production of colourless solutions of these methiodides on the ground of ionisation, and he concluded that iodine joined to nitrogen, oxygen, or sulphur in an aromatic ring formed a chromophoric group, since the methiodides of cyclic bases were coloured, whilst substances such as diphenyldimethylammonium iodide, which do not contain nitrogen in a ring, were colourless.

In connexion with a spectroscopic investigation on the action of bases on *isoquinoline* methiodide, carried out at the suggestion of Dr. Decker on lines similar to those employed by Dobbie, Lauder, and Tinkler (*Trans.*, 1903, **83**, 598) in their investigation on cotarnine, and by Dobbie and Tinkler on hydrastinine (*Trans.*, 1904, **85**, 1005), it was found that yellow *isoquinoline* methiodide gave spectra in chloroform solution entirely different from those of the substance in aqueous or alcoholic solution. Similar results were obtained in the case of pyridine, quinoline, acridine, and phenylacridine methiodides. In a letter written to Dr. Decker by the author in November, 1907, it was suggested that these phenomena might possibly be explained otherwise than by ionisation.*

From the spectra of pyridine methiodide in chloroform it was seen that the absorption in the visible part of the spectrum showed some resemblance to that of potassium tri-iodide (*Trans.*, 1907, **91**, 996), and it seemed possible that the colour of pyridine methiodide in chloroform solution might be due to the combination of two or

* An abstract from this letter has recently been published by Dr. Decker (*J. pr. Chem.*, 1909, [ii], **79**, 339).

more molecules of the substance by means of the iodine atoms, thus :



Some determinations of the molecular weights of these methiodides were therefore undertaken, the results of which were communicated to Dr. Decker, but were not published.

In a recent paper, Hantzsch (*Ber.*, 1909, **42**, 68) draws the conclusion that the colour of these methiodides is due to polymerisation. Although my examination of these alkyl iodides is not yet complete, it is thought advisable to publish the results so far obtained.

In support of the view that colour is due to polymerisation, Hantzsch gives the following results of molecular-weight determinations of phenylacridine methyl halides by the ebullioscopic method.

	M. W. in		M. W. calculated.
	Alcohol.	Chloroform.	
Chloride	263	$\begin{cases} 327 \\ 338 \end{cases}$	305·6
Bromide	341	$\begin{cases} 424 \\ 421 \end{cases}$	350·0
Iodide	362	$\begin{cases} 1161 \\ 1120 \end{cases}$	397·0
		$397 \times 3 = 1191 \cdot 0$	

From these results it is seen that in chloroform the methiodide is termolecular, and that the bromide and chloride are slightly associated.

The following results were obtained by the author.

A. Molecular Weights by the Ebullioscopic Method.

Phenylacridine Methiodide in Chloroform.

Substance.	Solvent.	E.	M. W.	
			Found.	Calc.
0·4896 gram	45·1 grams	0·033°	1204	397
			$397 \times 3 = 1191$	

This result is in agreement with those given by Hantzsch, showing that the iodide in chloroform is termolecular.

Quinoline Methiodide in Alcohol.

Substance.	Solvent.	E.	M. W.	
			Found.	Calc.
1·3460 grams	15 grams	0·38°	277	271

At this concentration in alcohol this substance appears to be uni-molecular. More probably, however, from the colour, the solution

contains a mixture of polymolecular and unimolecular iodide, of which some of the latter is dissociated.

Owing to the slight solubility of the methiodides in chloroform, it is impossible to carry out other molecular-weight determinations in this solvent.

B. Molecular Weights by the Cryoscopic Method.

Determinations of molecular weights by the cryoscopic method, employing diphenylamine, have been undertaken, since the methiodides are insoluble or only sparingly soluble in the ordinary solvents used in such determinations. In some cases water was employed as solvent.

Pyridine Methiodide.—This substance was obtained colourless by crystallisation of alcohol (compare Hantzsch, *loc. cit.*). It is, however, strongly coloured when dissolved in chloroform or when molten.

Molecular Weight in Diphenylamine.

	Substance.	Solvent.	$\Delta t.$	M. W.	
				Found.	Calc.
(i)	0.3465 gram	24.38 grams	-0.15°	833	221
(ii)	0.5935 „	24.38 „	-0.24	892	221

The mixture so obtained is of a yellow colour.

In this case the substance appears to be in the quadrimolecular condition.

Molecular Weight in Water.

	Substance.	Solvent.	$\Delta t.$	M. W.	
				Found.	Calc.
(i)	0.2500 gram	18.88 grams	-0.22°	111	221
(ii)	0.4142 „	18.88 „	-0.34	119	221

In solution (i) the substance is apparently completely dissociated; both solutions are colourless.

Quinoline Methiodide: Molecular Weight in Diphenylamine.

	Substance.	Solvent.	$\Delta t.$	M. W.	
				Found.	Calc.
(i)	0.1434 gram	22.94 grams	-0.13°	423	271
(ii)	0.5709 „	22.94 „	-0.34	644	271

The solution is of a red colour. On the addition of alcohol and water, diphenylamine is precipitated, and a colourless solution of the methiodide is obtained.

In Water.

	Substance.	Solvent.	$\Delta t.$	M. W.	
				Found.	Calc.
(i)	0.2098 gram	15.26 grams	-0.19°	134	271
(ii)	0.6325 „	15.26 „	-0.46	166	271

In (i) the solution is colourless, and the substance is apparently completely dissociated.

In (ii) the solution is yellow, and probably contains some polymolecular modification with unimolecular, some of which is dissociated.

Phenylacridine Methiodide: Molecular Weight in Diphenylamine.

	Substance.	Solvent.	$\Delta t.$	M. W.	
				Found.	Calc.
(i)	0.1300 gram	20.11 grams	- 0.13°	438	397
(ii)	0.4070 „	20.11 „	- 0.26	685	397

Both solutions apparently contain mixtures of unimolecular and polymolecular modifications.

From these results it appears that the substances are polymerised in chloroform and diphenylamine solution, and since these solutions, like the solids, are strongly coloured, it seems possible that the substances in the solid state are either polymeric modifications or solid solutions of polymolecular compounds in unimolecular. In the case of the pyridine alkyl iodides, however, which are colourless in the solid state, but coloured in various solvents, it is probable that the substances are unimolecular in the solid condition, but polymerised in certain solutions.

The view that the solids are mixtures of two forms receives support from the fact that the colour of the substance is largely dependent on the temperature. Thus, if the solids or solutions are heated, the colour is greatly intensified, whilst if cooled in liquid air the colour is greatly diminished (compare Hantzsch, *loc. cit.*).

It might be expected that heating would decompose the polymolecular modifications, since it has been shown that potassium tri-iodide is decomposed on heating (Trans., 1908, **93**, 1611).

By the addition of potassium iodide to the aqueous solutions of the methiodides, the colour is intensified. In this case the dissociation is diminished by the addition of the iodide ion, and the substance apparently polymerises.

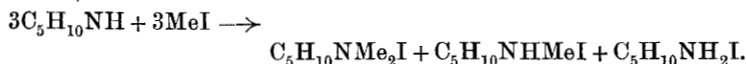
For the sake of comparison a determination of the molecular weight of a colourless substituted ammonium iodide in diphenylamine solution was carried out.

Tetrapropylammonium iodide (a 3 per cent. solution in diphenylamine) gave M.W. = 1362 (calculated M.W. = 312). Hantzsch (*loc. cit.*) also points out that dimethylammonium chloride in chloroform solution, although colourless, is strongly associated.

If the colour of the alkyl iodides of bases containing nitrogen in an aromatic ring is due to polymerisation, this colour may be due either to

the production of heavy molecules, the vibration of which brings the absorption into the visible part of the spectrum, or that the extra double bonds or ring formations, produced by the polymerisation, are responsible for a vibration, which, with that due to the linking in the aromatic nucleus, produces an absorption in the visible region of the spectrum.

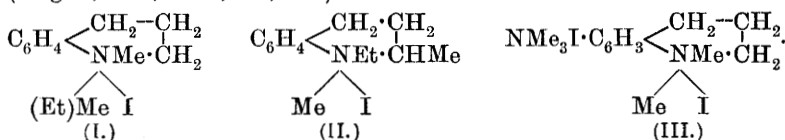
The latter theory receives support from the fact that the alkyl iodides of compounds containing nitrogen in a reduced ring are colourless. Thus piperidine and methyl iodide react with great violence when mixed together according to the following equation (Hofmann, *Ber.*, 1881, 14, 660):



These substances are all colourless, and give colourless solutions in water and in chloroform.

In addition, the methiodides of tetrahydroquinoline compounds are colourless.

The following compounds among others have been prepared by various investigators, and obtained colourless: Kairolin methiodide and ethiodide (I) (Wedekind, *Annalen*, 1901, 318, 110; Claus and Stegelitz, *Ber.*, 1884, 17, 1331). 2-Methyl-1-ethyltetrahydroquinoline methiodide (II) (Möller, *Annalen*, 1887, 242, 321); and the substance derived from aminokairolin by the action of methyl iodide (III) (Ziegler, *Ber.*, 1888, 21, 862).



Although this substance contains two iodine atoms, one is attached to nitrogen in a side-chain, and the other to nitrogen in a reduced ring; it is therefore colourless.

On the other hand, in the case of the alkaloids, cinchonine and quinine, which contain a piperidine and a quinoline nucleus, the monoalkyl iodides in which the iodine is attached to the piperidine nitrogen are colourless, whilst, as would be expected, the dialkyl iodides are coloured.

The action of various solvents on the hydriodides of bases was investigated as follows. Hydrogen iodide was passed into chloroform solutions of pyridine, quinoline, and isoquinoline. Yellow solutions were obtained, which, on shaking with water, gave colourless solutions. A similar loss of colour was noticed with an acridine solution. The hydriodides thus show the same phenomena as the alkyl iodides, and in the yellow solutions are probably polymolecular.

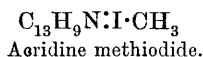
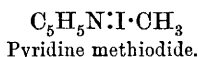
It is possible, however, that the coloured hydriodides and alkyl iodides of these cyclic ammonium bases differ in constitution from the corresponding methochlorides and colourless salts.

Quinoline combines with the various iodine derivatives of methane as follows :

One molecule of quinoline and one molecule of methyl iodide unite to produce quinoline methiodide, a yellow substance. Two molecules of quinoline unite with one molecule of methylene iodide to produce quinoline methylene iodide or methylenediquinoid hydriodide, a yellow substance (Rhousopoulos, *Ber.*, 1883, 16, 880). Three molecules of quinoline and one molecule of iodoform give methanetriquinoid hydriodide, which is colourless (Rhousopoulos, *Ber.*, 1883, 16, 202). In the two latter compounds, in addition to the structures implied by their names, it is possible that the iodine atoms are attached to the nitrogen by double bonds, thus :



in which case the alkyl iodides might be written :

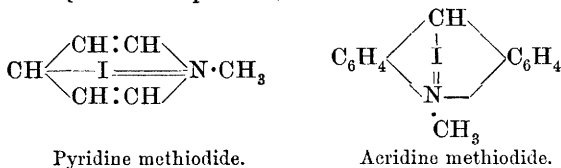


(compare Cain's ammonium chloride formula).

Or it is possible that the colour of the alkyl iodides is due to a tautomeric change between the two forms :



Other structural formulæ which might account for the colour of these iodine compounds are possible, such as



From the results so far obtained, however, the explanation of the colour afforded by polymerisation appears the most satisfactory.

If it can be proved that the colour is due to polymerisation alone, it might be found that many other substances owe their colour to the presence of a certain amount of a polymeric modification mixed with excess of unimolecular substance. Further experiments in this connexion are in progress.

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