SUMMARY.

(a) The behaviour of the aldazines as bases was examined in the first place by attempting preparations of a series of salts of seven typical aldazines. It was found:-

(i) That aliphatic aldazines did not yield salts but either decomposed at once in the presence of moisture and acid to give the corresponding aldehyde together with the hydrazinium salt, or, under anhydrous conditions, polymerised readily in the presence of acid, the products then often forming salts.

(ii) That aromatic aldazines formed simple and complex salts.

(iii) That "mixed" azines, containing one mol. of each of aromatic aldehyde and of acetone condensed per mol. of hydrazine, readily formed simple salts.

A complete series of complex salts of three aromatic aldazines was prepared and their properties compared. Several new simple salts of these aldazines, and of "mixed" azines were prepared, and the structural formula of one of the salts of a "mixed" azine was established. A co-ordination compound of one of the azines was prepared.

(See Table A below for a complete list of new compounds prepared).

(b) Experimental evidence has, for the first time, been given for the presence of an aldazinium ion in solution.

(c) The order of magnitude of the ionization constant as a base of one of the aldazines has been established.

(d) A preliminary kinetic investigation of the hydrolysis of the hydrochloride of one of the aldazines has been made, and a mechanism for the hydrolysis has been proposed.

TABLE A.

Common Chemical Name of Compound	m.p. °C	Number of Page on which preparation is given
Benzaldazine chloroantimonite	156 - 157°	44
Salicylaldazine "	175 - 182°	44
Anisaldazine "	198 - 200°	45
Benzaldazine bromoantimonite	179 - 180°	45
Salicylaldazine "	192 - 193°	47
Anisaldazine "	216 - 218°	47
Benzaldazine iodo-antimonite	172 - 190°	48
Salicylaldazine "	211 - 212°	48
Anisaldazine "	214 - 215°	49
Benzaldazine chlorobismuthite	200 - 206°	49
Salicylaldazine "	213 - 220°	49
Anisaldazine "	236 - 237°	50
Benzaldazine bromobismuthite	229 - 234°	50
Salicylaldazine "	ca. 227°	51
Anisaldazine "	244 - 245°	51
Benzaldazine iodobismuthite	228 - 236°	51
Salicylaldazine "	246 - 253°	52
Anisaldazine "	235 - 238°	52
Benzaldazine chlorostannate	217 - 225°	41
Salicylaldazine "	212 - 220°	42
O-nitro-benzaldazine "	185 - 190°	43
Benzaldazine bromostannate	218 - 225°	43
Anisaldazine "	240 - 242°	44
1 Stannic chloride. 2 salicylaldazine	224 - 231°	52
Benzaldazine hydrogen sulphate	160 - 161°	38
Salicylaldazine " "	178 - 179°	39
Anisaldazine " "	202 - 203°	39
Salicylaldazine hydrobromide	211 - 213°	38
N-benzylidene-N'-isopropylidene-hydrazinium bromide	135 - 136°	39
N-o-hydroxybenzylidenehydrazinium-N'-isopropylidene bromide	178 - 178°	40
N-benzylidene-N'-isopropylidenehydrazinium iodide	107 - 108°	40
N-o-nitrobenzylidene-N'-isopropylidene-zinium bromide	156 - 158°	41

S U M M A R Y.

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I. INTRODUCTION.

Hydrazine, N_2H_4, condenses readily with aldehydes or ketones forming (i) hydrazones (containing one molecule of aldehyde or ketone condensed per molecule of hydrazine and (ii) aldazines and ketazines (containing two molecules of aldehyde or ketone respectively condensed per molecule of hydrazine). Hydrazine is primarily a weak monoacid base ($pK_b = 7.93$ at 25°C[1]), although some salts with hydrogen halides, stable only in the solid state, have been prepared where it functions as a di-acid base.

Studies in the salt forming properties of hydrazine were initiated in the Chemistry Department of the University of Cape Town by the late Professor W. Pugh in 1952. Before the work described in this thesis was commenced he had already prepared a series of hydrazinium salts of the complex halogeno-acids of tin, antimony and bismuth[2,3], as well as compounds presumed to be the chlorostannates of dimethyl ketazine and of heptan-4-one hydrazone[4]. Work was also in progress on the preparation of the bromostannates and bromostannites of hydrazine, of dimethylketazine and of pentan-3-one hydrazone, the results of which were later published[5]. Thus although some compounds presumed to be the complex salts of ketazines had been isolated, no attempts were made to prove their formulation, and no attempts had been made to prepare the corresponding aldazinium salts. A survey of the literature revealed that the hydrochlorides of benzaldazine[6] and of anisaldazine[7] had been reported, again without proof of formulation, and that a compound corresponding to anisaldazinium hexachlorostannate was obtained by Shoesmith and Slater[7] on reducing anethole nitrosochloride in chloroform solution with stannous chloride and concentrated hydrochloric acid. No structural formula was suggested by the authors for this "addition" compound, as it was then named, and no evidence has previously been obtained for the existence of the aldazinium ion.

The present work was undertaken in order (i) to make a survey of the salt-forming properties of the aldazines in general (ii) to try to find some direct evidence for the existence of the aldazinium ion, and (iii) to attempt to obtain the ionization constant as a base of at least one of the aldazinium bases. After several aldazinium salts had been prepared it was observed that in the presence of moisture and acid the ion was readily decomposed by hydrolysis, giving two molecules of aldehyde and one of hydrazine. It was decided to attempt a kinetic investigation of the rate of this hydrolysis for at least one of the salts, and to suggest a possible mechanism for its occurrence.

To obtain as comprehensive a survey as possible of the salt forming properties of the aldazines the following azines were selected as bases:- acetaldazine, n-propaldazine, n-butaldazine and crotonaldazine and the aromatic azines benzaldazine, salicylaldazine and anisaldazine. Attempts were made to prepare and compare their chloro- and bromo-stannates, chloro-, bromo- and iodo-antimonites and bismuthites. In order to determine whether the aldazines (as is the case of the parent hydrazine) could sometimes act as di-acid bases, some simple sulphates and halides were also prepared.

Spectrophotometric methods were used to investigate the existence of the benzaldazinium ion, in order both to obtain a measure of the basic strength of benzaldazine, and to study the mechanism of the hydrolysis of its simple hydrochloride to benzaldehyde and hydrazine.

The aromatic aldazines were found to yield halides, sulphates and a complete series of the complex salts, whereas the aliphatic ones gave either oily products at -50°C or below (which decomposed rapidly at room temperature) or, in some cases, crystalline products of variable composition showing different degrees of polymerisation to have occurred.

In all the simple salts of the aldazines which were prepared the base was found to be monoacidic, even when an excess of acid was used in the preparation of the salt.

During the course of these preparations some simple salts of "mixed" azines (containing one molecule each of aromatic aldehyde and of acetone condensed per molecule of hydrazine) were isolated. Since these were prepared from acetone, the aromatic aldehyde, hydrazine and the halide acid, there was some doubt as to their structure. As Mannich[8] had shown that aldehydes and ketones could condense together with a primary or a secondary amine to form a base, which could often lose a second molecule of water forming a ring-closed base, it was considered necessary to show that the supposed salts of the "mixed" azines were not salts of similar Mannich bases, formed by such a condensation with hydrazine replacing the primary or secondary amine. The evidence in support of this is discussed in Chapter II, page 10.

When attempting to make a chlorostannate of acetaldazine, a crystalline compound of constant composition and melting point, and of high molecular weight was isolated. The structure of this polymerised compound appears to be complex and is discussed on page 8.

It has also been shown that the tendency which hydrazine displays to act as an electron donor in the formation of complexes is also shown by the aldazines. The assumption has been made, in the case of hydrazine, that both nitrogen atoms act as donors. Although simple salts in which the hydrogen ions are co-ordinated to both nitrogen atoms do not exist in solution, it is interesting to note that hydrazine in co-ordination with metallic ions appears to act principally as a bidentate molecule. In the case of the aromatic aldazines this property of the nitrogen atoms of donating electrons appears to be retained, as under anhydrous conditions

it was found that these aldazines co-ordinated with stannic chloride, antimony trichloride, and with bismuth trichloride. Only one such compound, namely disalicylaldazine stannic chloride was prepared pure. This substance can be compared to $SnCl_2.2N_2H_4$, which has been reported by Franzen and von Mayer[9]. The structures of such compounds would provide a further field for investigation.

The results obtained by the spectrophotometric investigations showed the presence of the benzaldazinium ion in a solution of the azine in dioxan containing an excess of dry hydrogen chloride. Hammett and Deyrup's method[10] for determining the pK_b values of weak bases was modified in order to obtain a measure of the basic strength of benzaldazine. Although fairly constant results were obtained for the pK_b of benzaldazine it has been shown that its standard deviation was too high for accuracy. All that could be deduced from the results was that the pK_b for benzaldazine lies between the limits of 0.16 and 1.46. This deduction is discussed on page 23. The basic strength of the azine thus appears to be of the same order as p-nitroaniline, $pK_b = 1.11$[11], and as benzeneazodiphenylamine, $pK_b = 1.52$[11].

A preliminary kinetic study of the hydrolysis of benzaldazine hydrochloride revealed that it was acid catalysed, the rate of hydrolysis being directly proportional to proton availability. The reaction was found to be of the first order with respect to benzaldazine, but the rates of hydrolysis at varying water concentrations could not be determined. Thus although a tentative mechanism for the hydrolysis has been proposed, it has not been confirmed. In order to do this a more rigid exclusion of moisture, both from the solvent and from the spectrophotometric cells during readings, would be necessary.

II. THE EXISTENCE AND HYDROLYSIS OF THE AZINIUM ION.

(1) Preparations of aromatic aldazinium salts.

(a) Methods of preparation of complex salts.

The first attempts to prepare the complex aldazinium salts of benzaldazine, salicylaldazine and of anisaldazine were based on methods analogous to those used by W. Pugh[2,3,4] for some of the corresponding ketazinium salts. These methods involved working in aqueous or in alcoholic solution, using the appropriate aldehyde and the metallic halide together with the hydrazinium halide, or in some cases with hydrazine hydrate acidified with the concentrated halide acid. These methods were found to be mainly unsuccessful, although in the case of benzaldazine bromoantimonite (a successful preparation of which was made from antimony trioxide, hydrobromic acid, hydrazine hydrate and benzaldehyde dissolved in ether) by changing the solvent to ether the salt was obtained. It was found impossible to use ethanol as solvent as the aldazinium salts were decomposed by it, the hydrazinium salts being precipitated. The reasons why the complex aldazinium salts were not usually obtained pure by these methods appeared to be threefold. Firstly, they were more readily hydrolysed than the ketazinium salts, yielding hydrazinium salts, whose solubility in most solvents was not very different from those of the aldazinium salts. Thus mixtures were precipitated which were not easily separated. In the case of the above mentioned benzaldazine bromoantimonite the difference in solubility in ether between it and hydrazine hydrobromide was sufficient to allow of a separation. The fact that Shoesmith and Slater[7] had isolated anisaldazine chlorostannate in the presence of concentrated hydrochloric acid using chloroform as a solvent had indicated that the complex aldazinium salts would be comparatively stable in the presence of strong acids. This, however, was not always found to be the case, the salts of anisaldazine being more stable under these conditions than those of the other two azines. The second reason why the above mentioned methods of preparation were not

usually successful was that the aldazinium salts were found to be soluble in the aldehydes from which they were derived, and hence an excess of aldahyde had to be avoided, as even a small excess frequently caused the formation of an oily product. The third reason was the fact that the aldehydes and the metallic halides form addition compounds, which were often a source of impurity.

For these reasons in the methods finally evolved for the preparations, great care was taken to use exact stoichiometric proportions of the various starting materials, and either (i) to avoid the presence of moisture entirely, thus eliminating hydrolysis and obtaining a high yield or failing which (ii) to allow the presence of the minimum quantity of water (by using 47% hydrobromic acid or 58% hydriodic acid) but choosing by trial and error a solvent for the reaction in which the solubilities of the aldazinium and the hydrazinium salts were sufficiently different to allow of a separation.

In order to ensure the presence of exact stoichiometric proportions (especially to avoid excess aldehyde) it was found best to prepare the azine first. This could then be dissolved in a suitable solvent, in which the required metallic halide was also soluble, and a mixture of the two solutions treated with the halide acid. In some cases no suitable solvent for both the azine and the metallic halide could be found. In such a case it was found possible to use two different, but miscible, solvents. This was done in the preparation of benzaldazine iodoantimonite, where xylol and ether were used as solvents for the antimony tri-iodide and the benzaldazine respectively.

In most cases ether was found suitable as a solvent for benzaldazine, and xylol or nitrobenzene for the other two azines, which were insoluble in ether. The reasons why salts of salicylaldazine presented unusual difficulties can then be seen in that this azine was only appreciably soluble in hot solvents,

which increased the amount of hydrolysis in the presence of moisture, causing lower yields of the aldazinium salts. The antimony and bismuth halides, being insoluble in ether, necessitated the use of nitrobenzene as solvent. Salicylaldazine bromobismuthite was the only aromatic complex salt which was not obtained entirely pure. The reason for this was the great similarity in solubility in all solvents tried of the hydrobromide and of the bromobismuthite; it being found difficult to remove the last traces of the hydrobromide from the complex salt.

For the chloro-complex salts method of preparation which resulted in the best yield was to mix solutions containing stoichiometric proportions of the simple hydrochloride of the azine with the metallic chlorides in nitrobenzene solution, as this avoided both the presence of moisture and of excess acid. The hydrochloride of salicylaldazine, however, in contrast to its methochloride (readily obtained by Lamchen and Stephen[12]), was not obtained pure (see III(1) (g) page 53) and hence the above method could not be used for the preparations of the complex chloro-salts of this azine. The difficulty in preparing this hydrochloride lay in the low solubility of the parent azine in all cold solvents, combined with the observed fact that the simple hydrochlorides of benzaldazine and of anisaldazine were found to decompose readily on heating with the evolution of hydrogen chloride, which suggested the need to avoid the use of hot solvents. Other attempts to make this hydrochloride, using different starting materials and a wide variety of solvents were unsuccessful, the product being invariably contaminated with salicylaldazine. This difficulty did not exist in the case of the methochloride of the azine where no contamination was possible. The above method of utilising the simple hydrochloride of the azine as starting material could not be extended generally to the hydrobromides and hydriodides as these simple salts were found to be even more easily hydrolysed than the complex salts, and difficulty was

experienced in preparing them in good yield in a sufficiently pure state.

When the first attempts at preparing aliphatic aldazinium salts met with no success, it was considered likely that this might be due to two factors; the first being their supposed even greater susceptibility to hydrolysis than the aromatic ones; the second being the known readiness with which the aldazines polymerise in the presence of acid. Accordingly it was decided to exclude moisture even more carefully than was possible working in the apparatus previously used (shown in Figure XI, page 36a,) in which rubber stoppers had been employed, and to work at low temperatures. A new apparatus was constructed (shown in Figure VII, page 37a) in which the whole reaction, addition of reagents, passage of hydrogen chloride, precipitation, filtration and washing could be done at any desired temperature with the exclusion of all moisture. Only oily products, however, were obtained at room temperatures, whereas at temperatures of -50°C and below crystals were formed, which became oils on reaching room temperature. In order to test whether the ease with which the aldazines polymerise was a more important factor than the presence of moisture a sample of hydrazine chlorostannate was prepared, dissolved in the minimum of water and allowed to react with an excess of acetaldehyde with cooling. Even under these conditions polymerisation occurred and the crystals isolated were those of a chlorostannate of a ring closed base of empirical formula $C_{22}H_{40(42)}N_4O_6SnCl_6$. Although the structure of this compound was not worked out it appeared to be a chlorostannate of a base formed by the polymerisation of acetaldehyde together with hydrazine. The hydrazine was in combination in a ring formation as there was no "free" hydrazine available for reaction with iodate. An infra-red spectrum of the compound was examined, and from the lack of absorption peaks between 5.8μ to 6.1μ it was deduced that no ordinary C = O, C = C or C = N groups were present. Further, from the slight absorption

at 2.9μ the presence of an -OH was indicated, although =NH stretching absorption also occurs in this region, and differentiation between the two was not possible with the resolution of the particular instrument used, especially at such low wave lengths. It was noted, however, that the intensity of the band at 2.9μ decreased when the potassium bromide disc containing the substance was kept in a desiccator, which indicated that the band was due to water, which had been removed subsequently in the dry atmosphere. In order to determine whether this was water of crystallisation or a trace of surface water which might have been picked up when preparing the disc, the compound was heated for 2½ hrs. at 100°C under reduced pressure. Although a colour change to a yellow-brown occurred, there was no loss in weight, proving the absence of water of crystallisation. From these facts it was deduced that the oxygen present must be combined as in ethers, probably in a closed ring.

When attempting to prepare benzaldazine bromoantiminite from stoichiometric quantities of antimony bromide, hydrazine hydrate, 47% hydrobromic acid together with benzaldehyde in absolute ethanol solution yellow granular crystals of undecahydroazinium heptadecabromodiantimonite, $(N_2H_5)_{11}Sb_2Br_{17}$, were formed. These were identical with the product obtained by Pugh[3] on warming a mixture of hydrazine hydrobromide and antimony tribromide in concentrated aqueous solution to which was added an equal volume of methyl alcohol. Further, on attempting to make the corresponding benzaldazine iodoantimonite by an analogous method to that used for the above mentioned bromo-compound (namely using ethanol as a solvent) large red crystals of undecahydrazinium heptadecaiododiantimonite, $(N_2H_5)_{11}Sb_2I_{17}$, separated. The hydrazinium iodoantimonites reported by Pugh[3] were trihydrazinium hexaiodoantimonite and hydrazinium tetraiodoantimonite both of which were prepared without the use of alcohol as solvent.

(b) Simple salts of "mixed" azines, and evidence for their assigned structures.

When attempting to purify salicylaldazine tetrabromoantimonite, contaminated with unchanged salicylaldazine, by extracting with boiling acetone, pink leaflets, m.p. 177 - 178°C, separated on cooling. These were shown by analysis to have the empirical formula $C_{10}H_{13}ON_2Br$. As salicylaldazine hydrobromide, $C_{14}H_{13}N_2O_2Br$, has m.p. 211 - 213°C, it was clear that an altogether different salt had been formed. It appeared likely that a molecule of acetone had replaced a condensed molecule of salicylaldehyde in the azine

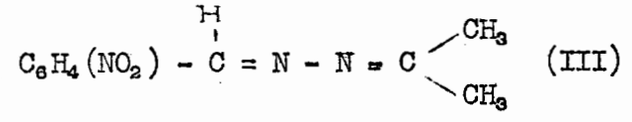
$$[C_6H_4(OH) - \overset{H}{\underset{|}{C}} = N - N = C(OH)C_6H_4]$$

forming the hydrobromide of a so-called "mixed" azine, II,

$$\left[\begin{matrix} H_3C \\ \diagdown \\ \quad C = N - N = C(OH)C_6H_4 \\ \diagup \\ H_3C \end{matrix}\right]$$

Two other similar salts were then prepared, one a hydrobromide from hydrazine hydrate in acetone acidified with 47% hydrobromic acid together with benzaldehyde, and the other a hydriodide made from benzaldazine in acetone acidified with 58% hydriodic acid. In order to show that these salts did contain a molecule of condensed acetone (as well as one of the original aldehyde) attempts were made to extract the free base from the hydriodide by ether extraction of an alkaline paste (potassium carbonate-water). The resulting extract contained benzaldazine and acetone, the former being isolated by evaporation in vacuo. The latter was detected by precipitation and subsequent separation of the 2:4 dinitrophenylhydrazones of acetone and of benzaldehyde obtained from the extract. The separation used was a modification of Rice, Keller and Kirschner's[13] method, (see page 35). The fact that benzaldazine and acetone were obtained in place of the free "mixed" azine , showed it to have been readily hydrolysed, a fact which is confirmed by Curtius and Pflug's[14] failure to isolate it from acetone hydrazone and benzaldehyde, (they also obtained benzaldazine and acetone). Having shown that the base of the hydriodide contained both condensed acetone and

benzaldehyde, it was next necessary to consider how the condensation had occurred. Two possibilities existed - either the base was the supposed "mixed" azine II, or it was a Mannich type base. The latter possibility seemed unlikely (i) in view of the fact that Mannich and Kather[8] had indicated that hydrazine salts do not condense with aldehydes and ketones in the same way as primary and secondary amines, and (ii) because of the ease with which the salts hydrolysed, which would have been unexpected had they been salts of Mannich bases. In order to confirm this conclusion it was decided to make in an analogous way to that used in preparing the above three salts of "mixed" azines, the salt of a "mixed" base which was known and stable, to liberate the base from the salt, and to compare the former with an authentic specimen of the base. As N-o-nitrobenzylidene-N'-isopropylidene hydrazine,



(III)

m.p. 67°C, had been reported[15], it was decided to choose this azine as base. The azine of o-nitrobenzaldehyde[15] was first prepared, and its chlorostannate made, to test whether the azine of this aldehyde would form salts readily. Then this azine in acetone was treated with 48% hydrobromic acid, and the precipitated salt proved to be the hydrobromide[6] of the required "mixed" azine (III). This salt, made into a paste with potassium carbonate and water, was extracted with ether. The free base, isolated in the usual way, had m.p. 67°, undepressed on mixing with an authentic specimen. This proved that it was not a salt of a Mannich base, and as the three above mentioned simple salts had been made in an analogous manner it was concluded that they, too, were salts of similar "mixed" bases.

(2) Spectrophotometric evidence of the existence of the aldazinium ion.

(a) Choice of method and solvent.

After a series of supposed aldazinium salts had been prepared it seemed desirable (i) to obtain some more direct evidence for the existence of the aldazinium ion, and also (ii) to try to obtain the ionisation constant as a base of at least one of the aldazines, namely benzaldazine.

The experimental methods considered were:- (i) a partition method, (ii) a potentiometric method, (iii) a conductivity method and finally (iv) a spectrophotometric method. The first was ruled out because of the susceptibility of the aldazinium salts to hydrolysis to the aldehyde and hydrazine. The final choice of method depended on finding a suitable solvent for the hydrochloride of benzaldazine, which, in common with the other aldazinium salts, was either unstable or insoluble in most organic solvents. However, pyridine, nitrobenzene and dioxan were found to dissolve this salt. The use of pyridine, a base, as solvent for the purpose of determining the basic strength of the azine was naturally impossible. The second solvent, nitrobenzene, was also excluded for use in the first three of the above mentioned methods, as the azine hydrochloride, although appreciably soluble on warming (possibly with decomposition) was sparingly soluble in the cold. It was considered likely that the solubility of the hydrochloride in cold nitrobenzene would be sufficient for the spectrophotometric method where only extremely dilute solutions need be employed. However, its optical density made its use as solvent unsuitable for the purpose required. A mixture of equal volumes cyclohexane and nitrobenzene was also shown to be unsuccessful for the same reason.

Thus the choice of solvent was restricted to dioxan. Owing to its low di-electric constant and low specific conductivity the conductivity method had to be excluded. Of the two remaining methods the spectrophotometric one was chosen as the solubility of

the salt in dioxan was considered sufficient for this but not for a potentiometric one. It was further ascertained that the optical density of pure dioxan made its use as solvent for the above purpose permissible, in that the maximum absorption of benzaldazine [ε_{max} = 36,000 at 300 mμ in alcoholic solution[16] and ε_{max} = 36,400 at 302 mμ in dioxan solution (this work)] occurred at a wave length where dioxan was completely transmittant. (See Figure XIV, page 54a).

The spectrophotometric method for determining basicity, first used by Hammett and Deyrup[10], is based on the fact that many organic bases have absorption curves which differ appreciably from those for their corresponding cations. Thus if the absorption curves for benzaldazine, for its simple hydrochloride, and for the benzaldazinium ion in a suitable solvent, could be plotted, then not only would this furnish direct evidence for the first time for the existence of an aldazinium ion, but it would also provide data from which the relative proportion of free base to ion in the solution of the hydrochloride could be calculated. This ratio, $\frac{C_B}{C_{BH^+}}$, together with a knowledge of the acidity function, Ho, of the solution of the hydrochloride, would enable the basic strength, pK_b, of the azine to be calculated by Hammett and Deyrup's equations[10]:-

$$pK_b = Ho + \log \frac{C_{BH^+}}{C_B} \quad \text{.....} \quad \text{Equation I}$$

$$pK_b = Ho + \log \frac{(K - K_B)}{(K_{BH^+} - K)} \quad \text{.....} \quad \text{Equation II}$$

In these equations:-

C_{BH^+} = molar concentration of the benzaldazinium ion.

C_B = molar concentration of benzaldazine.

K = molecular extinction coefficient of benzaldazine hydrochloride.

K_B = molecular extinction coefficient of benzaldazine.

K_{BH^+} = molecular extinction coefficient of benzaldazinium ion.

Ho = negative logarithm of the acidity of the solution in terms of a basic indicator.

The values for K, K_B and K_{BH^+} for use in Equation II refer to solutions in the same solvent at a fixed wave length.

A fuller definition of Ho, first introduced by Hammett and Deyrup[10], is given in Appendix I, page 70. The derivation of Equation II from Equation I is shown in Appendix II, page 72. 72 74

Thus if K, K_B and K_{BH^+} could be obtained, and if Ho were known for the particular solvent in use, then it should be possible to utilise Equation II in order to find pK_b. Although the acidity functions, Ho, of varying concentrations of hydrogen chloride in dioxan had been obtained by Braude[17] by spectrophotometric methods, there was some doubt as to their reliability, because James and Knox[18] had subsequently obtained consistently higher results by conductivity methods. As these authors, however, had not measured Ho over a range of hydrogen chloride concentrations, Braude's figures were used for substitution in Equation II, and a final allowance made to the value of pK_b obtained for the variation in Ho. In order to use this method for obtaining the pK_b of benzaldazine reliable values for K, K_B and K_{BH^+} were also required.

(b) <u>The absorption curve for the benzaldazinium ion.</u>

The first attempt to obtain an absorption curve for the benzaldazinium ion, was based on the expectation that that of the metho-chloride of benzaldazine, namely

$$\left[C_6H_5 - \underset{H}{C} = \overset{+}{\underset{CH_3}{N}} - N = \underset{H}{C} - C_6H_5\right]Cl^-$$

would be almost identical. The presence of the methyl group on the nitrogen atom would not be expected to alter the absorption appreciably. Thus attempts were made to prepare the above named metho-chloride. These attempts, described on page 55, were unsuccessful in that no crystalline product was obtained. However, a sample of pure methyl-hydrazine hydrochloride was prepared with the intention of dissolving a known weight of it in dioxan, and of adding the stoichiometric quantity of benzaldehyde, and of then determining the absorption

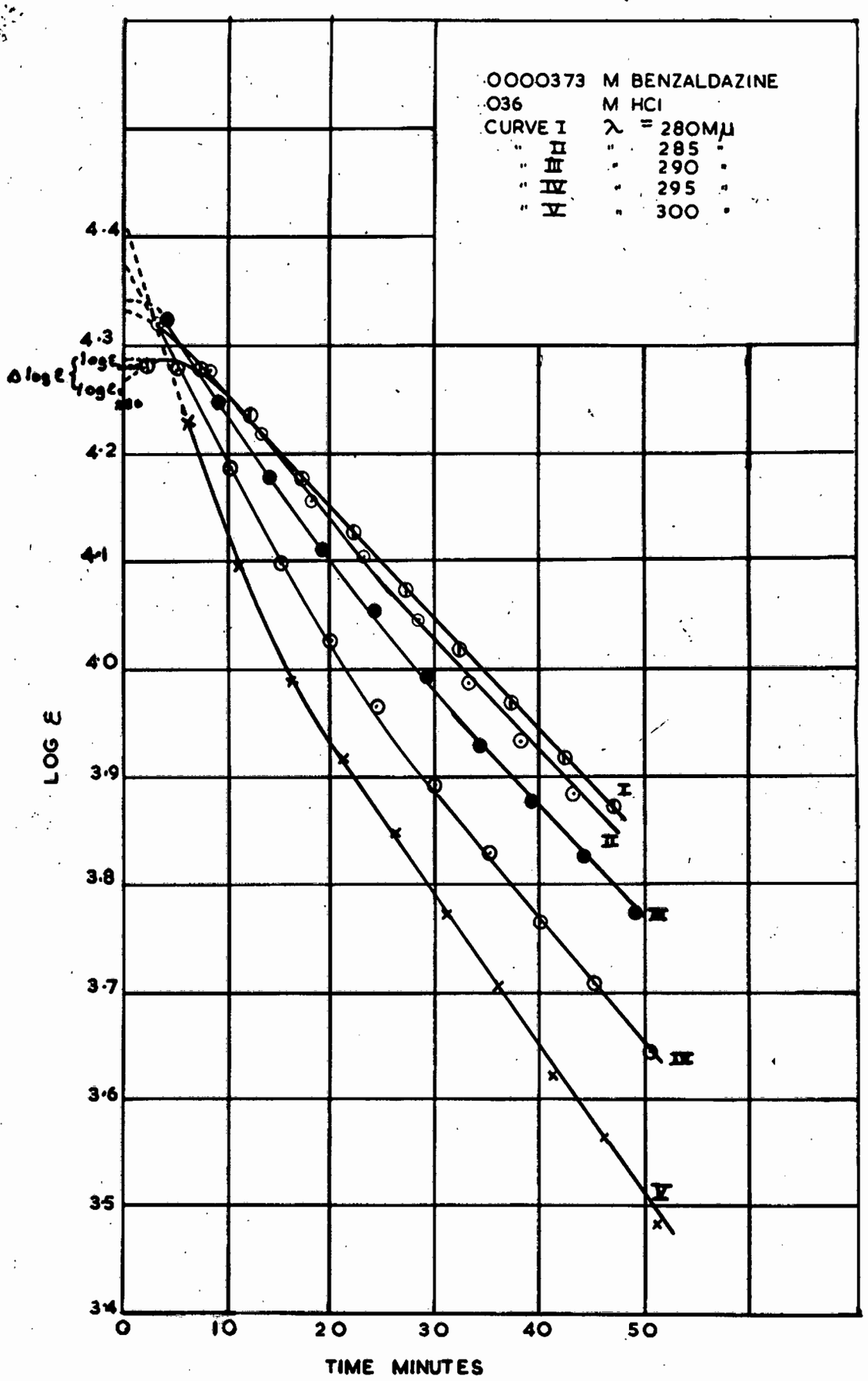

0.0000373 M BENZALDAZINE
0.36 M HCl
CURVE I λ = 280 mμ
" II " 285 "
" III " 290 "
" IV " 295 "
" V " 300 "
Δ log ε
log ε
log ε
LOG ε
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
0
10
20
30
40
50
TIME MINUTES

FIGURE I

spectrum of the resulting solution. This could not be done in practice as the methylhydrazine hydrochloride proved to be insufficiently soluble in dioxan. However, to its saturated solution in dioxan a slight excess of pure benzaldehyde was added, and the absorption curve of the mixture plotted. This curve showed a maximum at 282 mμ (see Table III, page 56), the actual height of the peak not being significant in this case, as the concentration of the solution was unknown.

This method of determining the absorption curve for the azinium ion having failed, an alternative method was attempted. It was considered possible that, if in a solution of benzaldazine in dioxan, the hydrogen ion concentration could be increased sufficiently, the azine would be partly or wholly converted to the corresponding ion. Accordingly an attempt was made to obtain the absorption curve of a solution of benzaldazine in dioxan, containing a known concentration of dry hydrogen chloride. It was found, however, that in such a solution, at a fixed wave length, the extinction changed comparatively rapidly with time, indicating the occurrence of a chemical reaction. In order to attempt to determine the nature of the reaction, its rate was studied. It was observed that during the first few minutes the graph of log extinction against time for a fixed wave length was a curve, thereafter a straight line. (See Figure I for a typical example of the curves obtained, in this case for a 0.036 molar solution of hydrogen chloride in dioxan). These curves were extrapolated to zero time, and it was hoped that the values of the extinction thus obtained for the solutions containing the higher concentrations of hydrogen chloride, would be those of the benzaldazinium ion. After repeating the whole procedure at different concentrations of hydrogen chloride it was noted that (i) the error in extrapolation to zero time was high due to the shape of the curve obtained for the initial twelve minute period, and (ii) different values of the extinction at zero time, ε_0, for the same azine concentration at a fixed wave length, were obtained. Curve I,

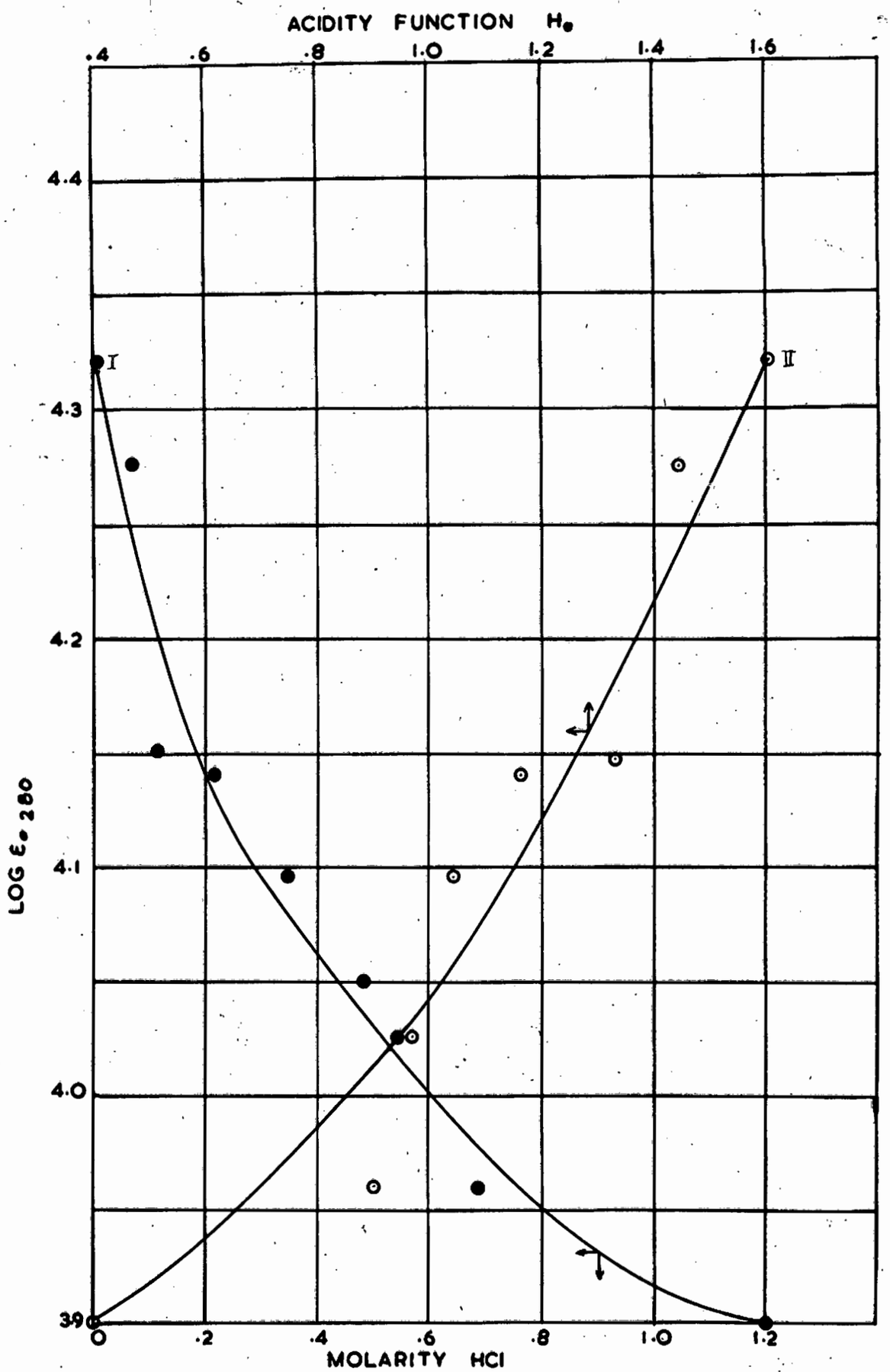

ACIDITY FUNCTION H_o
.4
.6
.8
1.0
1.2
1.4
1.6
4.4
4.3
4.2
4.1
4.0
3.9
LOG ϵ_{280}
I
II
0
.2
.4
.6
.8
1.0
1.2
MOLARITY HCl

FIGURE II

Figure II, shows the plot of log $\varepsilon_{o\,(280\ m\mu)}$ against the molarity of hydrogen chloride in dioxan, and Curve II in the same figure the plot of log $\varepsilon_{o\,(280\ m\mu)}$ against the acidity function of the solution. Owing to the inaccuracy in obtaining ε_o both curves can be regarded only as "trend" curves. They do show, however, that ε_o does not reach a definite limiting value as the concentration of hydrogen chloride was increased to the maximum obtainable with any accuracy from the practical point of view. Thus it was clear that the molecular absorption curve for the azinium ion was not obtainable by the above mentioned method.

However, from the plots of time against log ε, at a fixed wave length, for solutions of the azine in dioxan containing hydrogen chloride, complete curves of log ε at a fixed time over the significant wave length range were drawn. Each curve thus obtained represented the value of the absorption at a particular time. A typical series of curves are shown in Figure III, (for a 0.341 molar solution of hydrogen chloride), from which it was apparent that a new absorbing species was being formed during the first few minutes of reaction, and that this species was then undergoing a further reaction. It also appeared that the latter was a reaction of the first order (with respect to the azine concentration) as the plot of log extinction $(\alpha \log \frac{a}{a - x})$ against time was a straight line. Another significant point emerged on examination of the results. Namely, at certain wave lengths the molecular absorption of the new species was greater than that of the azine. This was concluded from the observation that at these wave lengths there was a rise in absorption with time, i.e. on formation of the new absorbing species (see Table VII, page 60). This meant that the latter could not be benzaldehyde or its hydrazone which, over the wave length range under consideration had considerably lower molecular absorption coefficients. This is shown on page 57 , Table IV where the molecular absorption coefficients of both substances in dioxan solution are given.

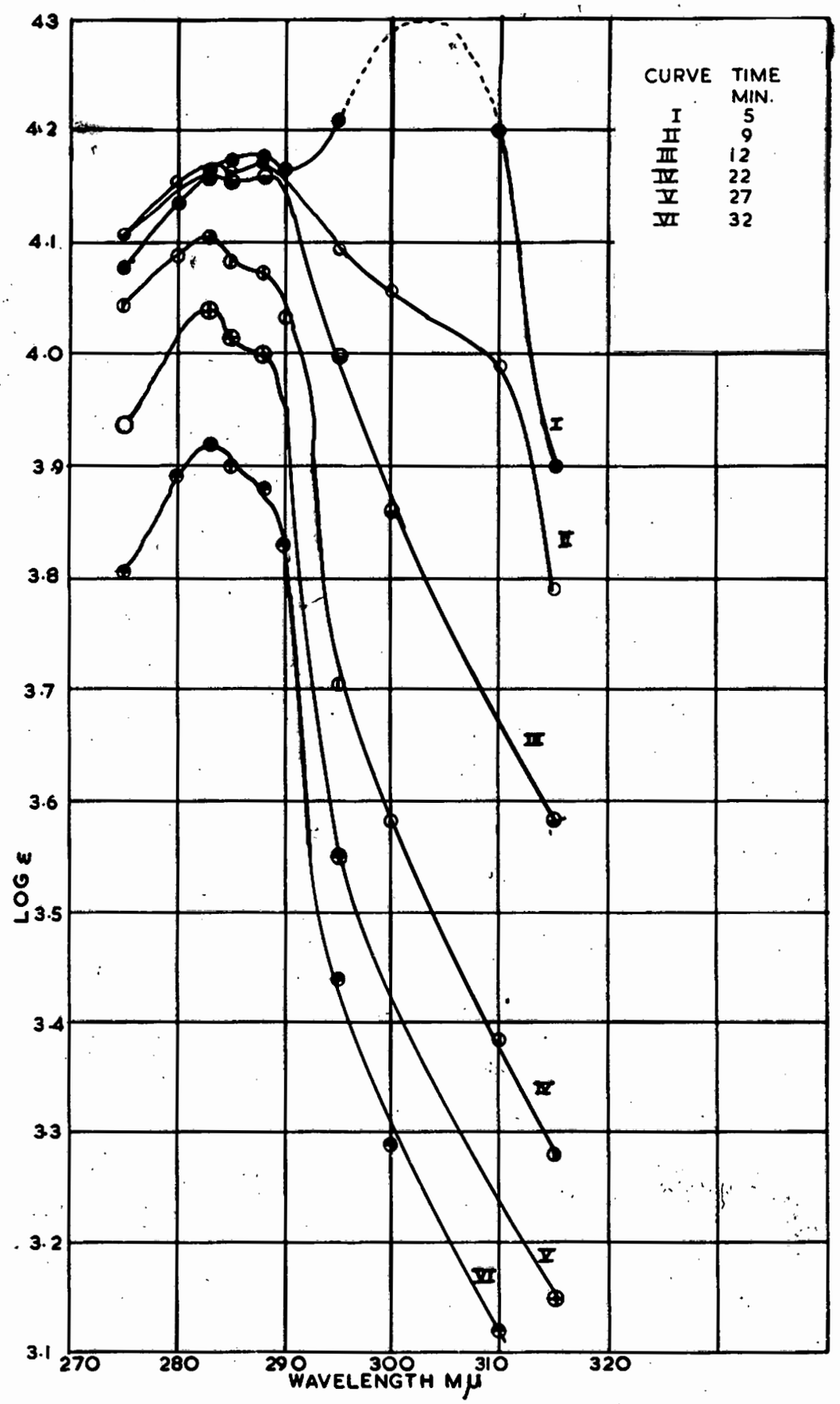

CURVE TIME MIN.
I 5
II 9
III 12
IV 22
V 27
VI 32
I
II
III
IV
V
VI
LOG ε
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
270
280
290
300
310
320
WAVELENGTH MμI

FIGURE III

The assumption was then made that the new absorbing species was the azinium ion. The reasons for this were:- (i) The molecular extinction maximum of this ion, and the wave length at which it occurred should not be very different from that of the parent azine, as it would have essentially the same amount of conjugation. Further, Braude[19] has shown that the maximum possible extinction coefficients of molecules can be calculated from molecular dimensions, and that these extinction maxima depend on the effective "chromophore area" of the molecule. As for the azine and for its ion the effective "chromophore areas" should be of the same order of magnitude, their absorption maxima should also be similar. (ii) The final maximum shown by this new absorbing species was at a wave length of 285 mμ, i.e. close to the wave length at which the maximum absorption for the solution of methylhydrazine hydrochloride with benzaldehyde in dioxan occurred. (See page 15). (iii) The possibility of a solvent shift of the azine curve due to the presence of the hydrogen chloride, was ruled out as an explanation of the reaction occurring, because this would have been an instantaneous effect. Such a solvent shift of the original azine absorption curve was not discarded entirely, as a possibility existed that the results obtained reflected a combination of two effects, i.e. an immediate shift of the original azine extinction curve, due to the presence of the hydrogen chloride, followed by a reaction. Such a shift could be due to a change in the dielectric properties of the solvent, on introduction of the polar hydrogen chloride molecules, with a consequent change in optical properties and in solute-solvent interaction. In order to investigate the nature of the reaction occurring in the course of its first few minutes, the effect of increasing concentration of hydrogen chloride on the height of the maximum absorption attained by an azine solution of fixed concentration at a fixed wave length (280 mμ), was studied. This choice of wave length was made in that it was close to that at which the new absorbing species showed its maximum. From the results already obtained of the molecular extinctions, at 280 mμ,

at various time intervals, of solutions of fixed azine concentration, but varying hydrogen chloride concentration, the differences, $\Delta(\log \varepsilon)$ between $\log \varepsilon_{max}$ and $\log \varepsilon_0$ (obtained by extrapolation) for each run were plotted (i) against the molarity of the hydrogen chloride in the solution (Curve I, Figure IV) and (ii) against the acidity function, Ho, of the solution. (Curve II, Figure IV). From these curves it can be seen that the maximum rise in absorption increases with increased concentration of hydrogen chloride. Further this maximum rise in absorption bears an approximately linear relationship with the acidity function of the solution, substantiating the assumption that the reaction occurring in the first few minutes is the formation of the azinium ion. This is in contrast to the lack of correlation between ε_0 and the acidity function of the solution (see Curve II, Figure II, page 15a), indicating that the initial drop in absorption is, indeed, due to a solvent shift effect. The extent to which the absorption curve of the azine is lowered depends, thus, more on the molarity of the solution (see Curve I, Figure IV) than on its proton availability.

The above was taken as justification for the assumption that the new absorbing species was the azinium ion. However, it was still not directly possible to obtain its molecular extinction curve. This was due to the reaction which the ion was undergoing, in that the curves plotted at the various times represented curves for unknown concentrations of ion.

The following method was evolved for finding the molecular extinction curve for the azinium ion. Since after the first twelve minutes, when two absorbing species appeared to be present, presumably azine and azinium ion, the absorption curve assumed a definite shape and then simply dropped steadily with time, (see Curves IV to VI, Figure III, page 16a) it was tentatively assumed that these curves represented the true shape of that of the azinium ion. A method was sought for finding the "starting position" of these curves. It was noted that the molecular extinction curves of benzaldazine and of

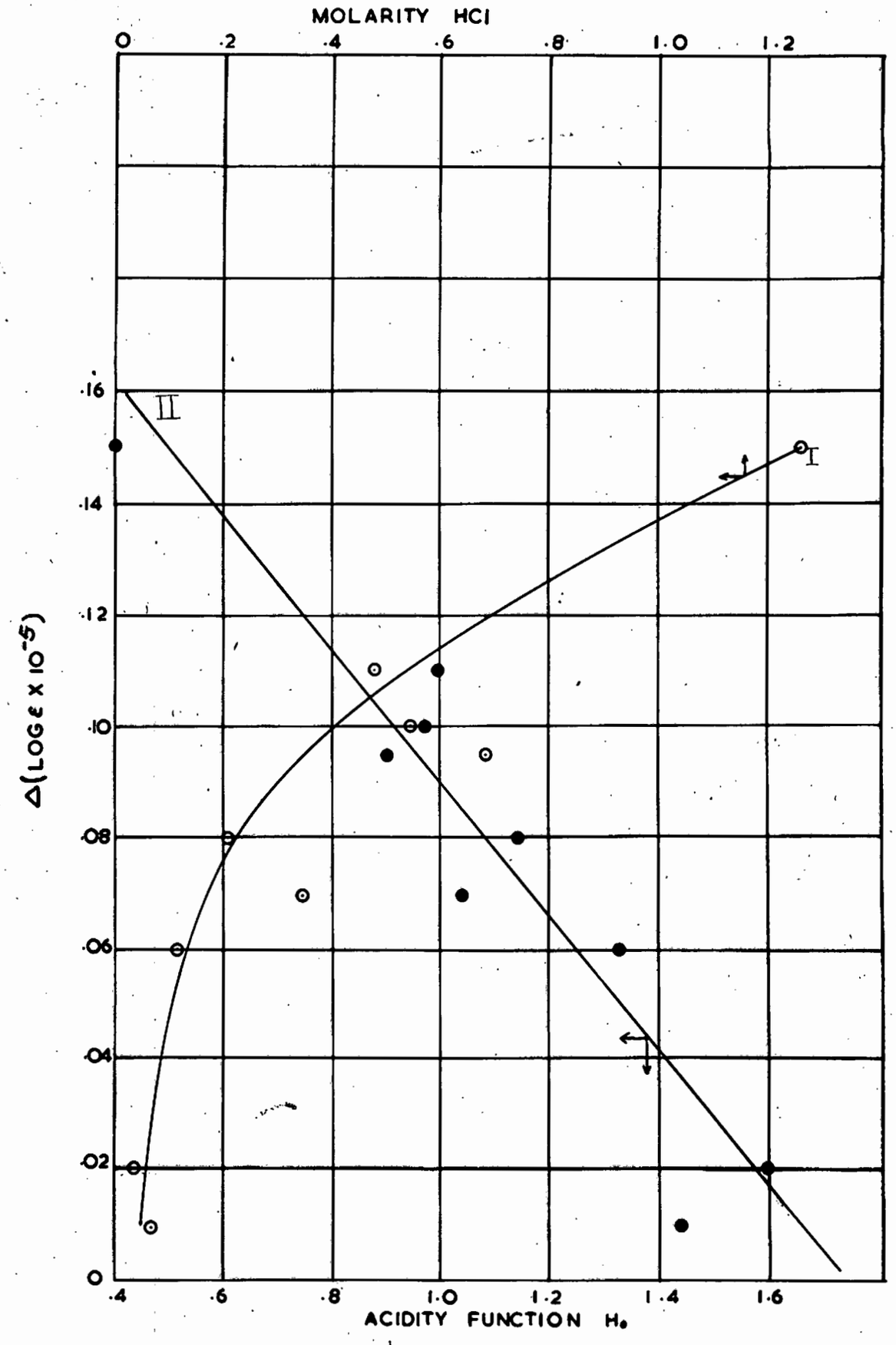

MOLARITY HCl
0
.2
.4
.6
.8
1.0
1.2
.16
.14
.12
.10
.08
.06
.04
.02
0
Δ(LOG ε X 10⁻⁵)
II
I
.4
.6
.8
1.0
1.2
1.4
1.6
ACIDITY FUNCTION H₀

FIGURE IV

its hydrochloride in dioxan solvent (see Curves I and II, Figure V, page 19a) cut at about 290 mμ. As this point must represent the wave length at which the azine and its protonated ion have the same absorption, all curves of mixtures of the same total concentration of azine and of its ion, must pass through it. Thus the "starting curve" for the azinium ion, which represents the curve for complete conversion of the azine to its ion, must also pass through this point. Hence if the latter could be found accurately, the curves for the azinium ion of unknown concentration could be adjusted to pass through it. However, the exact position of the point of cut of the absorption curves for the azine and for its hydrochloride was not definite, as the two curves were practically coincident over a wave length range of from 280 to 293 mμ. (See Curves I and II, Figure V, page 19a). To find the point of cut more accurately use was made of the following facts. At wave lengths at which the absorption of the azinium ion was higher than that of the azine, an immediate rise in the value of the extinction on the formation of the ion would be expected, whereas at wave lengths at which the absorption of the azinium ion is less than that of the azine, an immediate drop in the value of the extinction on the formation of the ion should occur. Thus the value of the wave length (294 mμ) at which there was no immediate rise or fall in extinction with time was taken to be that wave length for which the azine and its ion had the same absorption. The extinction curve for the benzaldazinium ion was then taken to be the curve obtained by adjusting any of the curves IV, V or VI, Figure III, page 16a, to pass through the point representing the value of the molecular extinction of benzaldazine at 294 mμ. The curve thus obtained was Curve III, Figure V. Curves IV and V , Figure V, were obtained by repeating the above procedure with the results obtained for the same concentration of azine but for molarities of hydrogen chloride of 0.682 and 1.262 respectively.

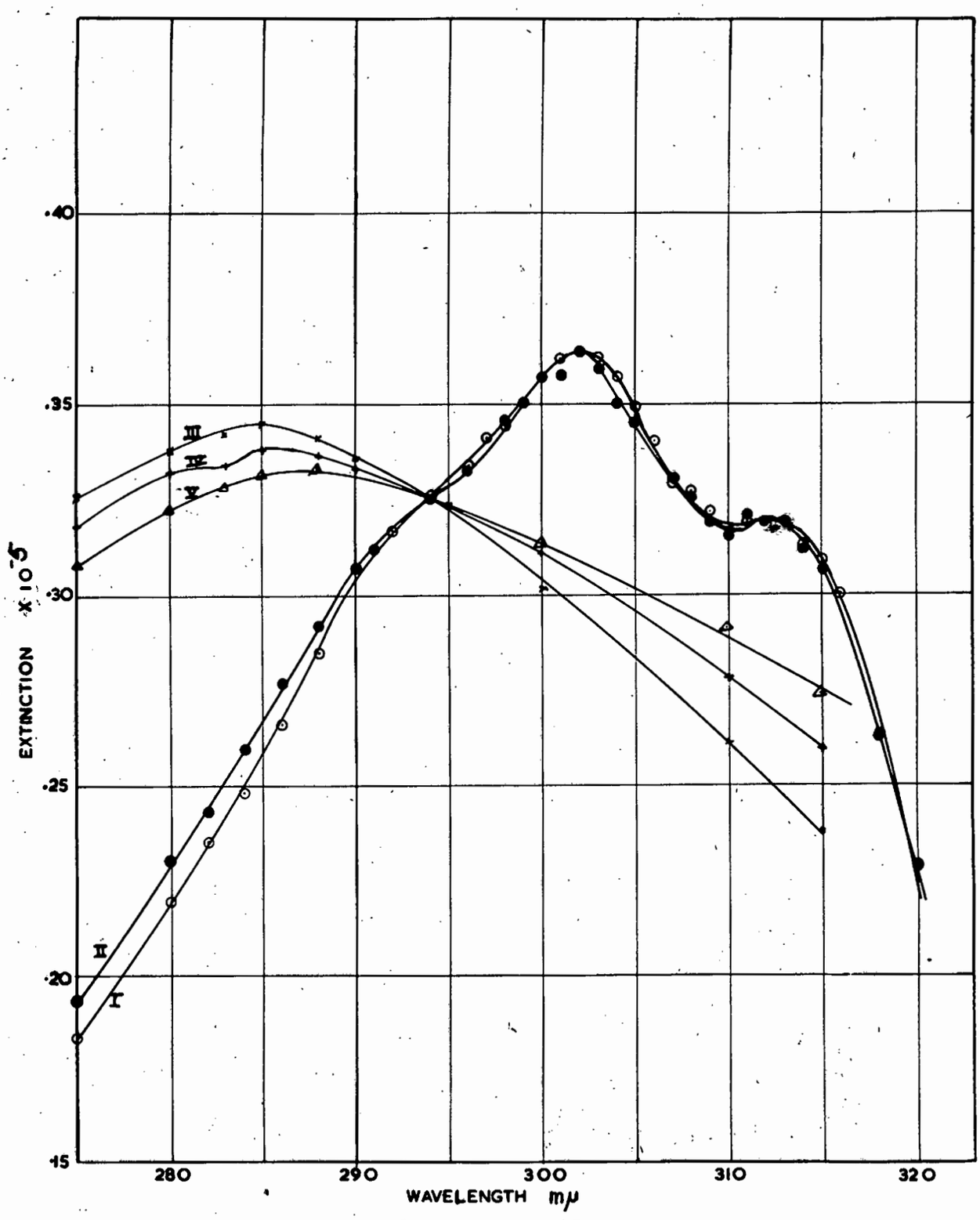

.40
.35
.30
.25
.20
.15
EXTINCTION X 10⁻⁵
280
290
300
310
320
WAVELENGTH mμ
I
II
III
IV
V

FIGURE V

(c) The absorption curves for benzaldazine and for its hydrochloride.

The absorption curves for benzaldazine and for its hydrochloride in dioxan solution were determined (Curves I and II, Figure V) and were found to be similar. This could be interpreted in three ways:-

(i) The azinium salt might exist in dioxan entirely as free azine and as hydrogen chloride, i.e. no benzaldazinium ion might be present. This would imply that the Curves I and II (Figure V) should be identical, and that the differences observed were fortuitous, or due to trace impurities. Both these possibilities were ruled out by, in the first place, determining many absorption curves on the same specimens, and, in the second place, determining further curves on specimens prepared on different occasions from different starting materials. Although the curves obtained were not always entirely coincident over the whole wave length range, it was apparent that the curve for the free azine was below that of its salt up to a certain wave length (between 290 and 297 mμ) within which range a point of cut for the two curves could be observed. At higher wave lengths the absorption of the salt was slightly lower than that of the free azine.

(ii) The second possibility was that the curves for the azine and for its ion might not differ materially. If this were the case the spectrophotometric method would have had to be abandoned, but as many examples were known where an organic base and its protonated ion showed appreciably different absorption curves (e.g. phenazine and its hydrochloride) this possibility was considered unlikely.

(iii) The third possibility was that the azine was such a weak base that in benzaldazine hydrochloride in dioxan the concentration of the benzaldazinium ion would be extremely low.

Thus it was obvious that if the basicity of the azine was to be determined by the method described above it would be necessary to plot the curves of the azine and its hydrochloride with the maximum accuracy. The following precautions were therefore taken in obtaining the Curves I and II, Figure V:-

(i) The concentration of the original azine solution was adjusted carefully so that all readings of extinction would be in the most sensitive part of the Beckman Spectrophotometric scale (i.e. between 0.2 and 0.9 extinction).

(ii) The wave length range was limited to that with least solvent or other interference.

(iii) The effect of changes in temperature by uneven heating due to the hydrogen lamp after the first few minutes was eliminated by controlling the temperature to within 0.5°C.

(iv) Readings were commenced at the same wave length (270 mμ) within five minutes of preparing the solution, in order to cut out variability due to solvent-solute interaction. It was found necessary to take these precautions, but variability of readings due to solvent evaporation was found to be insignificant when using dioxan as solvent. For the more volatile solvent, ethyl alcohol, such evaporation was more serious.

(d) <u>The determination of the ionisation constant as a base of benzaldazine, and a discussion of its validity.</u>

An approximate value for the ionisation constant, K_b, of benzaldazine was calculated by Hammett and Deyrup's Equation I (see page 13). Before substituting values for K, K_B and K_{BH^+} obtainable from Curves I, II, III, IV and V in Figure V, page 19a, it was necessary to decide the maximum wave length range that could be chosen with accuracy. Readings at wave lengths below 275 mμ could not be used as the standard deviations of the individual

readings for the molecular extinction of the azine and of its hydrochloride were almost double the standard deviations at higher wave lengths. (See Tables V and VI, pages 58 and 59). This was no doubt due to the fact that the solvent dioxan, although 100% transmittant at wave lengths greater than 297 mμ, absorbed slightly at lower wave lengths. (See Figure XIV, page 54a). Between wave lengths of 270 and 275 mμ the solvent was only between 65% and 85% transmittant, and hence solvent interference was to be expected in this range, resulting in less reproducibility in readings. At 294 m the azine and its hydrochloride had the same value for their molecular extinctions, and between 288 and 298 mμ the differences in extinction were so small as to be useless for the above mentioned method of calculation. At higher wave lengths than 298 mμ the curve of the azinium ion was not as reliable as for lower ones, as its shape was only reliable near its maximum, the lower portions being no doubt influenced by the presence of benzaldehyde or its hydrazone. Thus readings for K, K_B and K_{BH^+} were confined to the wave length range 275 to 288 mμ. (See Table XII, page 64A). The mean value of K_b thus obtained was 0.11 ± 0.035, the latter figure being the experimental standard deviation. This deviation of 0.035 reflected a greater accuracy than it was possible to obtain using the above method. Its reliability was checked by calculating the standard deviation of the value of K_b by the following general method.

If $y = f(x_1; x_2 \ldots\ldots)$

then $$S^2 y = \left[\frac{\partial f(x_1, x_2 \ldots\ldots)}{\partial x_1}\right]^2 S^2_{x_1} + \left[\frac{\partial f(x_1, x_2 \ldots\ldots)}{\partial x_2}\right]^2 S^2_{x_2} + \ldots\ldots$$

where S_y = true standard deviation of function y, which varies with $x_1, x_2 \ldots\ldots$

S_{x_1} = standard deviation of x_1

S_{x_2} = standard deviation of x_2

In the above case:-

$$K_b = \frac{K - K_B}{K_{BH^+} - K} = f(K, K_B, K_{BH^+})$$

$$\therefore \quad S^2_{K_b} = \left(\frac{\partial K_b}{\partial K}\right) S^2_K + \left(\frac{\partial K_b}{\partial K_B}\right)^2 \cdot S^2_{K_B} + \left(\frac{\partial K_b}{\partial K_{BH^+}}\right)^2 \cdot S^2_{K_{BH^+}} \quad \text{... Equation III}$$

Substituting values of K, K_B and K_{BH^+} at wave lengths of 275, 280, 282, 284, 286 and 288 mμ the mean of the values of S_{K_b} obtained was found to be 0.13 and at wave lengths of 275, 280, 282 the mean was 0.08 (see Table XIII, p. 66).

In order to work out pK_b for benzaldazine from equation I,

i.e. $pK_b = Ho + \log \frac{C_{BH^+}}{C_B}$, the value for Ho for dioxan containing a vanishingly small concentration of hydrogen chloride was required. This quantity, Ho, first introduced by Hammett is a measure of proton availability in non-aqueous solutions, its value decreasing with increasing protonavailability. Although Braude[17] has published the values of Ho for solutions of varying concentrations of hydrogen chloride in dioxan, there is some doubt as to the reliability of these values. James and Knox[19], using conductivity methods, found consistently higher results for Ho (for 0.1 molar hydrogen chloride in dioxan-water mixtures of varying proportions) than the corresponding ones given by Braude. In this work Braude's results have been utilised, but a final adjustment to the possible range of values of pK_b for benzaldazine has been made to allow for a possible higher value of Ho in accordance with James and Knox' results. Thus Braude's values of -Ho for solutions of varying concentrations of hydrogen chloride in dioxan were plotted against the molarity of the hydrogen chloride (Figure VI) and the curve obtained was extrapolated to zero hydrogen chloride concentration, giving the required value of Ho as 1.68. This value was now substituted in Equation I:-

$$pK_b = 1.68 + \log (.11 \pm .08) \quad \text{(Using Braude's value of Ho)}$$

i.e. $.16 < pK_b < .96$

As the possibility exists that Ho is higher, in accordance with the results of James and Knox at 0.1 molar hydrogen chloride, the upper limit for pK_b must be extended to 1.46.

i.e. $.16 < pK_b < 1.46$

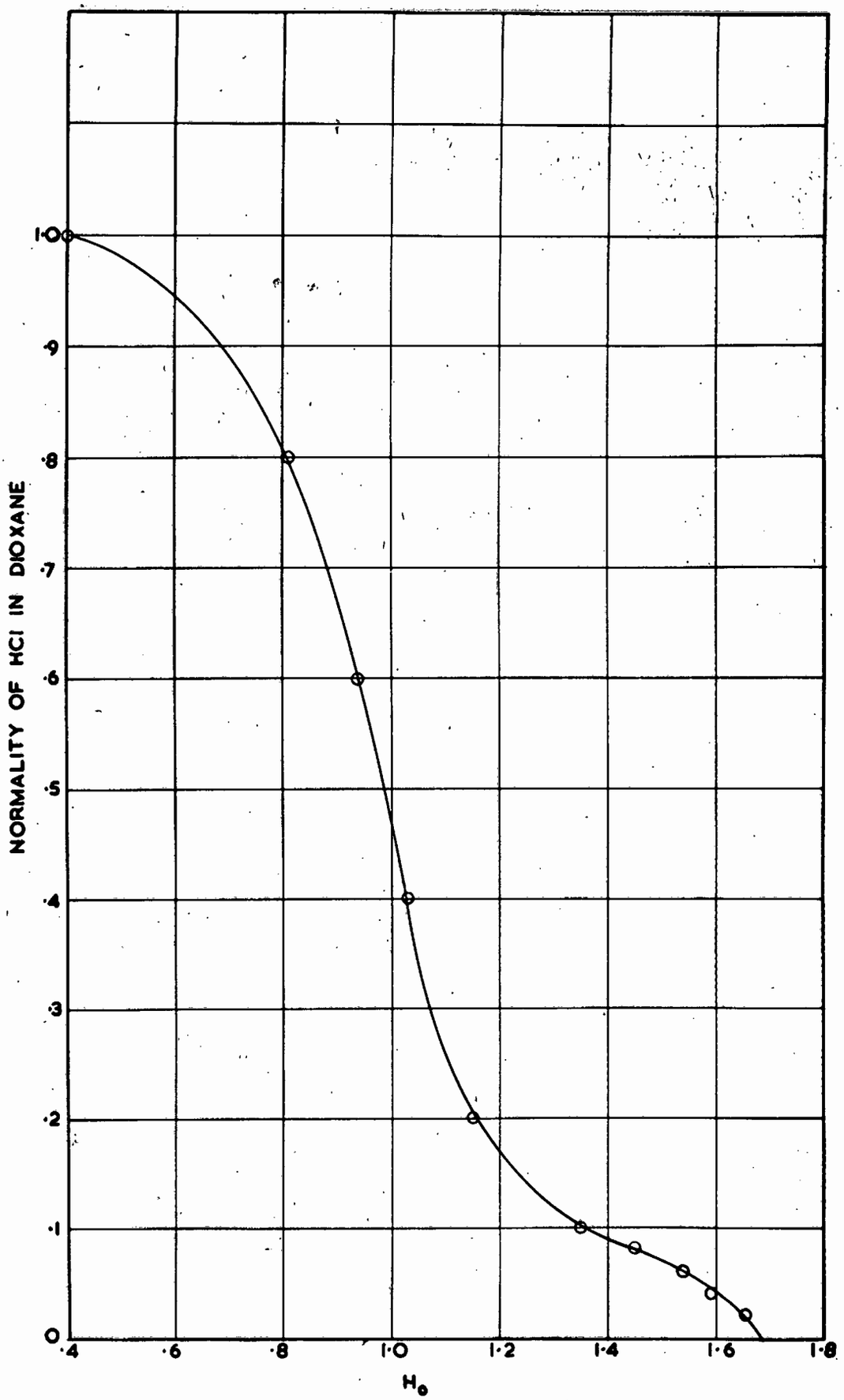

NORMALITY OF HCl IN DIOXANE
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
H₀

FIGURE VI

that the reaction was of the first order with respect to the azine concentration. The fact that at high acid concentrations (i.e. greater than 0.3 molar) the curve was no longer completely linear, did not necessarily mean a change in the order of the reaction, but was interpreted (see (a) above) as due to the formation of comparatively high concentrations of the hydrazone of benzaldehyde, the molecular extinctions of which would no longer be negligible. Similarly the shape of the log ε-time curve for the first twelve minutes of reaction was due to the presence of unchanged benzaldazine as well as of benzaldazinium ion.

The effect of different acid concentrations on the rate of the reaction was determined by measuring the rates at different molarities of hydrogen chloride, keeping the azine and the water concentrations the same. In order to obtain the specific velocity constants for the hydrolysis at various acid concentrations, the slopes of the corresponding log ε-time curves were required. Accordingly the curves shown in Figure IX were drawn. These represented the log ε against time curves for solutions of fixed azine concentration, but varying acid concentrations at the wave length of 295 mμ. This choice of wave length out of the five possible ones of 280, 285, 290, 295 and 300 mμ was made, as at the first three mentioned the absorption of the hydrazone of benzaldehyde formed affected the slopes of the log ε-time curves at the higher acid concentrations to a greater extent than at the last two wave lengths. Further 300 mμ was cut out as at this wave length the values of log ε dropped too low after a comparatively short time to fall on the more accurate part of the Beckmann spectrophotometeric scale. An examination of Figure IX showed that only on 0.48, 0.54 and 0.682 molar hydrogen chloride solutions did the log ε-time curves cease to be linear after about eighteen minutes. The specific velocity constants K, were obtained from the linear portions of the curves in Figure IX, from the relationship:-

$$K = \frac{-2.303}{\text{rate of change of log } \varepsilon \text{ with time}} \ \text{min}^{-1}$$

Hence the above method has not given an absolute value for the ionisation constant of benzaldazine, but has shown it to lie within the range:-

$$0.16 < pK_b < 1.46$$

(3) The mechanism of the hydrolysis of benzaldazine in the presence of acid.

(a) Determination of the nature of the reaction between benzaldazine and hydrogen chloride in dioxan solution.

As it was suspected that the reaction which had occurred when hydrogen chloride in dioxan was mixed with benzaldazine in the same solvent, was an hydrolysis to benzaldehyde and hydrazine, attempts were made to verify this as follows:- The rate of the reactions were measured, keeping the azine and the hydrogen chloride concentrations the same, but adding varying quantities of water. As can be seen from Curves I, II, III, IV and V, Figure VII, where the linear portions of the Curves I to V are parallel, the rate of the reaction was found to be independent of the water concentration. This could only mean either (i) that water played no part in the reaction, indicating that it was not an hydrolysis, or (ii) that water was already present in excess in the solvent, and hence that the added quantity of water did not influence the rate. To decide between these two possibilities the water content of the solvent dioxan was determined by Karl Fisher titrations, (see page 54). It was found that water was indeed present, its concentration being 0.44% (0.24 M) which would represent a large excess of water in comparison to the azine concentration in the dioxan, which was 10,000 times more dilute.

As the ease with which azinium salts hydrolyse in the presence of acid and water was well established, there was every indication that the reaction was indeed such an hydrolysis. This was confirmed by the results obtained on studying the rate of the reaction at varying acid concentrations. It was found that when the hydrogen chloride concentration was low (up to about 0.3 M) the plots for

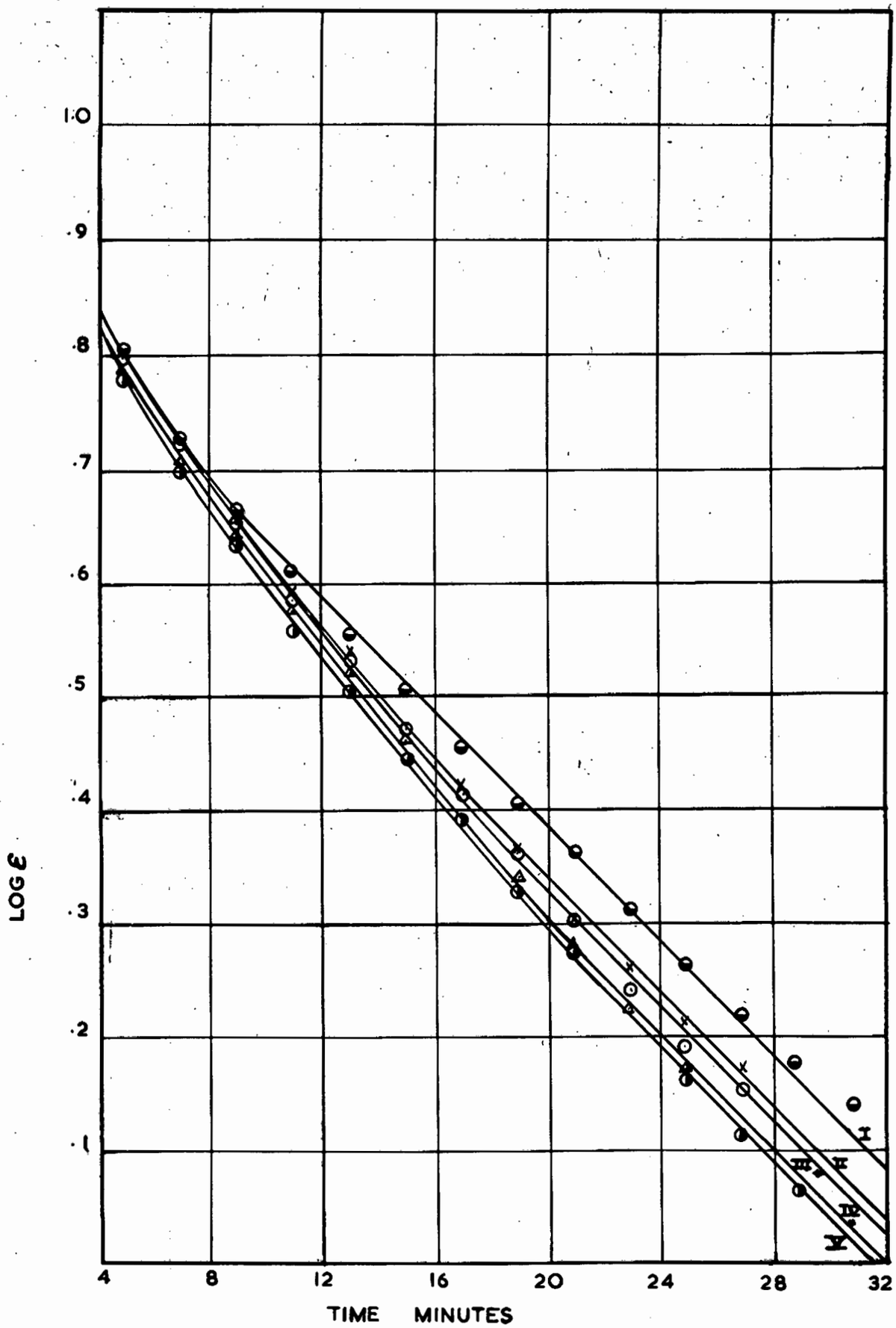


FIGURE VII

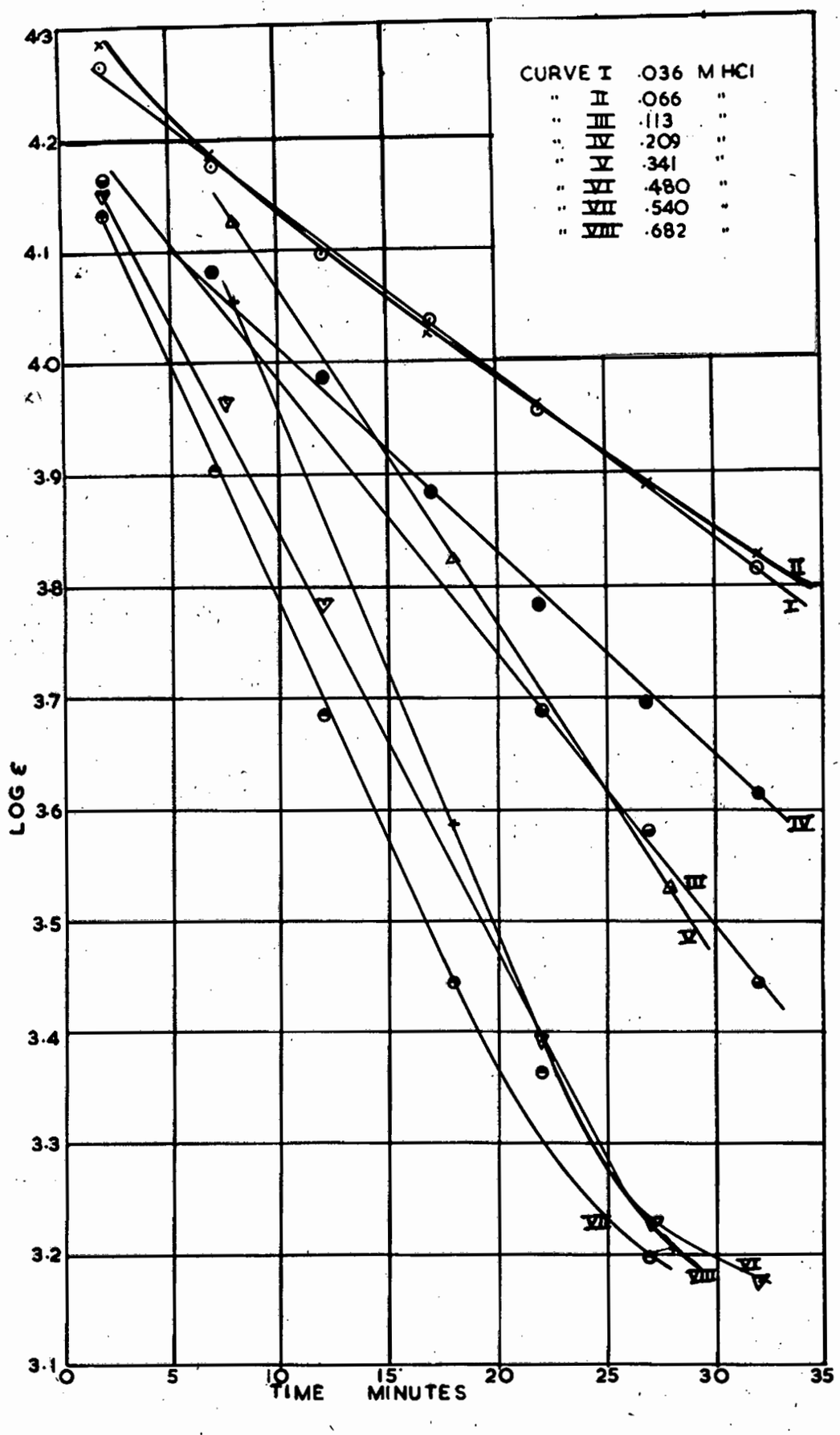

CURVE I .036 M HCl
" II .066 "
" III .113 "
" IV .209 "
" V .341 "
" VI .480 "
" VII .540 "
" VIII .682 "
LOG ε
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
0
5
10
15
20
25
30
35
TIME MINUTES

FIGURE IX

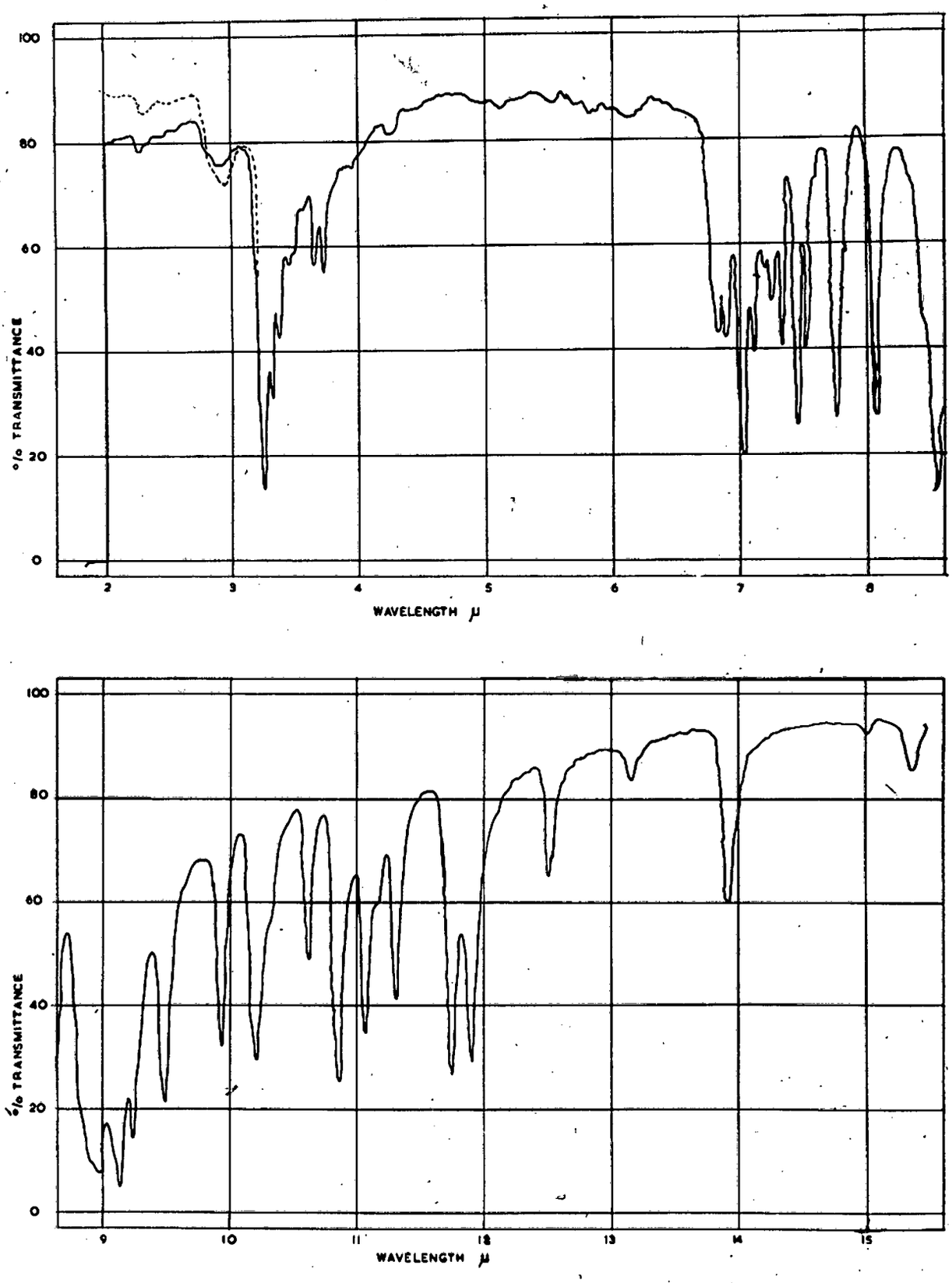

100
80
60
40
20
0
% TRANSMITTANCE
2
3
4
5
6
7
8
WAVELENGTH μ
100
80
60
40
20
0
% TRANSMITTANCE
9
10
11
12
13
14
15
WAVELENGTH μ

FIGURE X

that the reaction was of the first order with respect to the azine concentration. The fact that at high acid concentrations (i.e. greater than 0.3 molar) the curve was no longer completely linear, did not necessarily mean a change in the order of the reaction, but was interpreted (see (a) above) as due to the formation of comparatively high concentrations of the hydrazone of benzaldehyde, the molecular extinctions of which would no longer be negligible. Similarly the shape of the log ε-time curve for the first twelve minutes of reaction was due to the presence of unchanged benzaldazine as well as of benzaldazinium ion.

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$$K = \frac{-2.303}{\text{rate of change of log } \varepsilon \text{ with time}} \ \text{min}^{-1}$$

No obvious relationship was noted between the molarity of the acid and the specific velocity constants, but the relationship between the acidity function of the solution and the corresponding specific velocity constant, K, is shown in Table XV. In the first column of this table the molarity of the hydrogen chloride in the dioxan is given; in the second is the corresponding value of the acidity function, Ho, as determined from the curve in Figure VI, page 23a, which was drawn from figures published by Braude[16]; in the third column is the specific velocity constant, K in min^{-1}, as determined from the linear portions of the corresponding curves in Figure IX; in the fourth column the logarithm of K is recorded; and finally in the last column the sums of log K and Ho are shown, and appear to be approximately constant. As Ho is also a logarithmic function this can be expressed in the following way:-

$$\log K - \log h = \log C \qquad \text{..... Equation IV}$$

$$\text{or } \frac{K}{h} = C \qquad \text{..... Equation V}$$

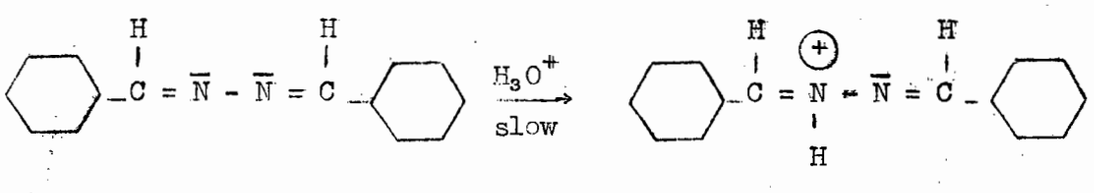
where h (see Equation VIII, appendix I, page 72.) is a direct measure of proton availability. Thus the specific velocity constant, K, is directly proportional to proton availability.

(c) Suggested mechanism of the hydrolysis of benzaldazine to hydrazine and benzaldehyde.

With the solvent containing 0.44% water it was not possible to study the effect of changes in water concentration on the rate of hydrolysis.

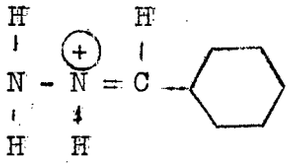
As, however, it was shown in Section II (2) that the azinium ion was formed as the first stage in the hydrolysis, the following is suggested as a possible mechanism for the reaction:-

In the first place benzaldazine reacts with the solvated proton to form the benzaldazinium ion:-



I II

The hydrazone would now react with a solvated proton at the nitrogen atom having the higher electron density, i.e. at the nitrogen atom attached by the double bond to the carbon atom, forming V,



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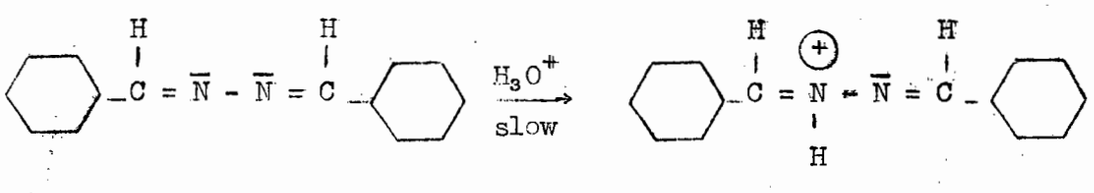
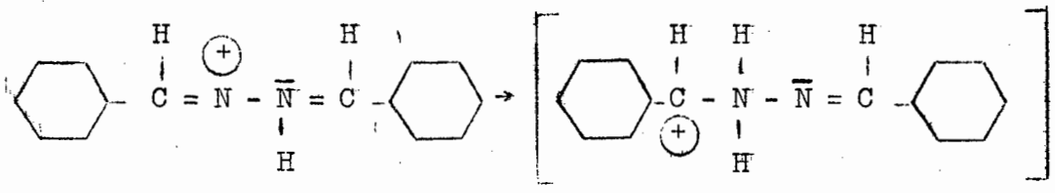
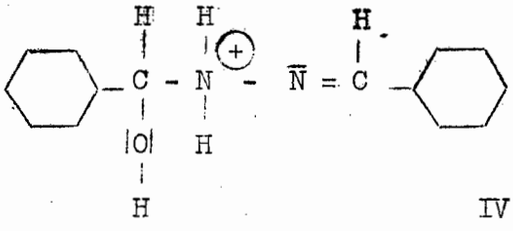


I II

This reaction is a "slow" one, in that its rate is measurable, as shown by the shape of the rate curve during the first ten minutes of hydrolysis. (See Figure I, page 14a). As the formation of an ion is usually instantaneous, this result appears surprising. However, it may be due to a steric effect, caused by the complexity and size of the benzaldazine molecule, in that the ion may only be formed when the proton approaches the nitrogen atom in certain directions. Once the azinium ion is formed, the nitrogen atom carrying the positive charge would tend to draw electrons from the neighbouring carbon atom at its double bond:-

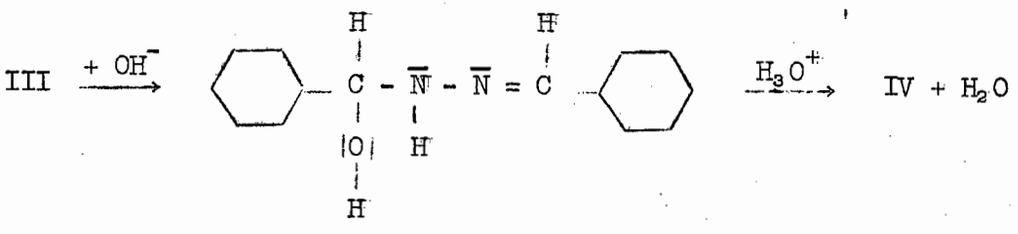


At this stage there appear to be two ways in which III can be converted to

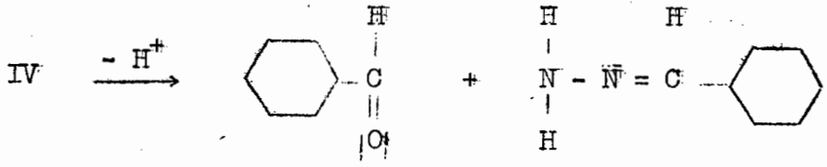


IV

Either this conversion occurs in one stage by means of a water molecule attacking III at the electron deficient carbon atom, or it occurs in two stages, (the initial attack being made by an hydroxyl ion) thus:-



The next stage of the hydrolysis consists of the loss of a proton, together with the formation of benzaldehyde and benzalhydrazone.



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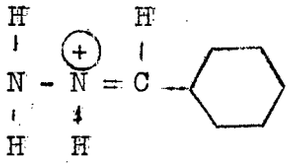

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III. EXPERIMENTAL.

(1) Preparations of aromatic aldazinium salts.

(a) Purity of reagents and solvents utilized.

The aromatic azines used as starting materials in the preparations of the series of salts, were made from hydrazine hydrate (60%; 1 mol.) and the stoichiometric quantity of aldehyde (2 mols.) in alcoholic solution. Benzaldazine[13], anisaldazine[14] and o-nitrobenzaldazine[12] were crystallised from ethanol, and salicylaldazine[13] from chloroform. The aliphatic azines, acetaldazine[15], n-propaldazine[16], n-butaldazine[16], and crotonaldazine[17] were prepared by the methods indicated in the references given.

Hydrazine hexachlorostannate was prepared by fractional crystallisation of a mixture of stannic chloride pentahydrate and a saturated aqueous solution of hydrazine monohydrochloride.

The stannic chloride used for the various preparations had been purified by low pressure distillation, and was completely anhydrous, while the other metallic halides used were C.P. grade.

The solvents xylol, benzene and cyclohexane were dried by refluxing with sodium and were kept in containers with sodium wire, while the nitrobenzene was freshly distilled. The ether was distilled from concentrated sulphuric acid and also kept over sodium.

(b) Methods of analysis.

An essential preliminary treatment for the removal of aldehyde was necessary before the aldazinium salts prepared below could be analysed completely. This was effected in two ways. All the simple and some of the complex salts were readily hydrolysed by acids with the evolution of the aldehyde. Thus 5N hydrochloric acid was used for the hydrolysis prior to a sulphate, hydrazine, bismuth or tin determination, and 2N sulphuric acid for a halogen or antimony estimation. The period of hydrolysis varied - the salts of benzaldazine being decomposed more rapidly than the corresponding ones of anisaldazine, whilst those of salicylaldazine were the most

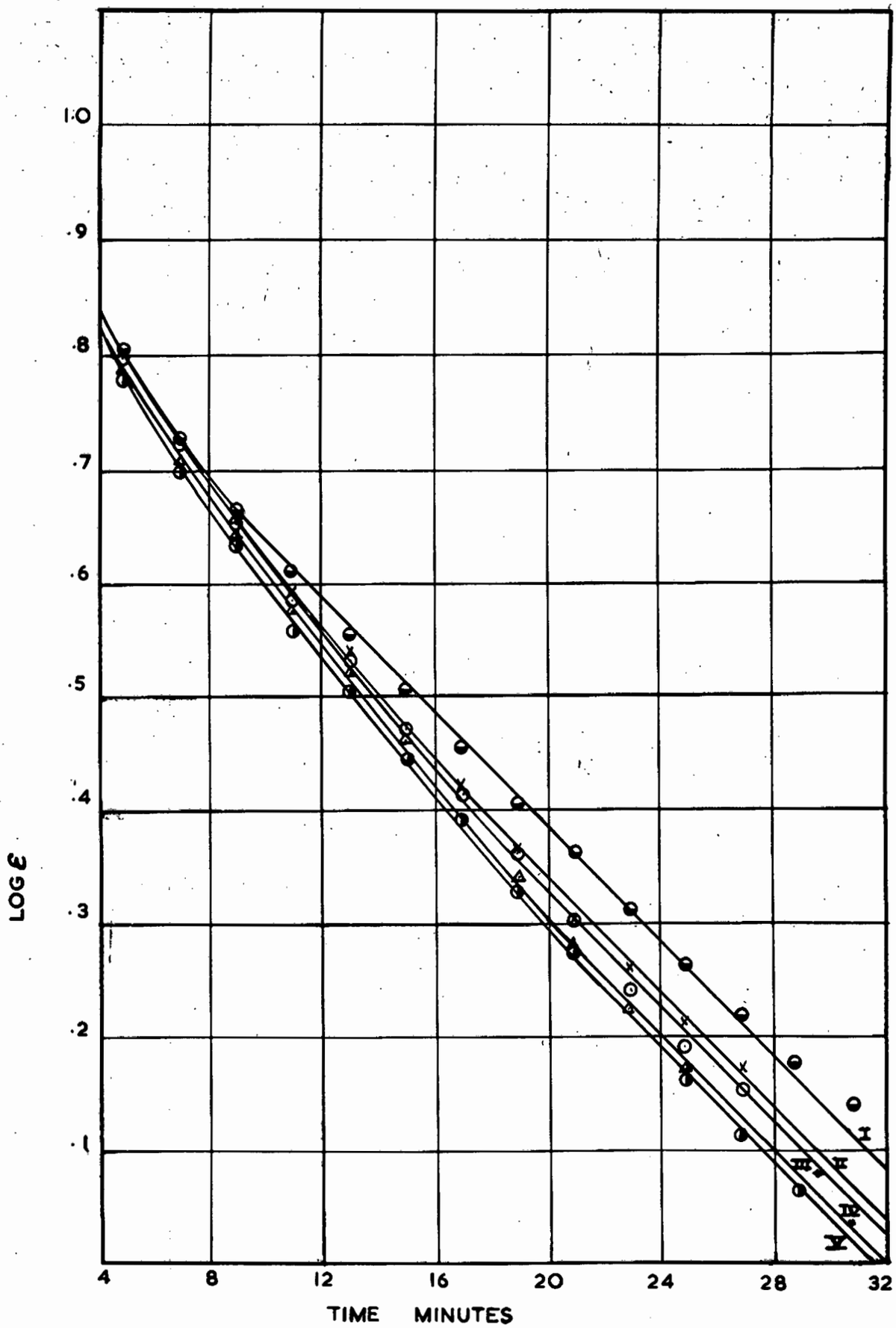
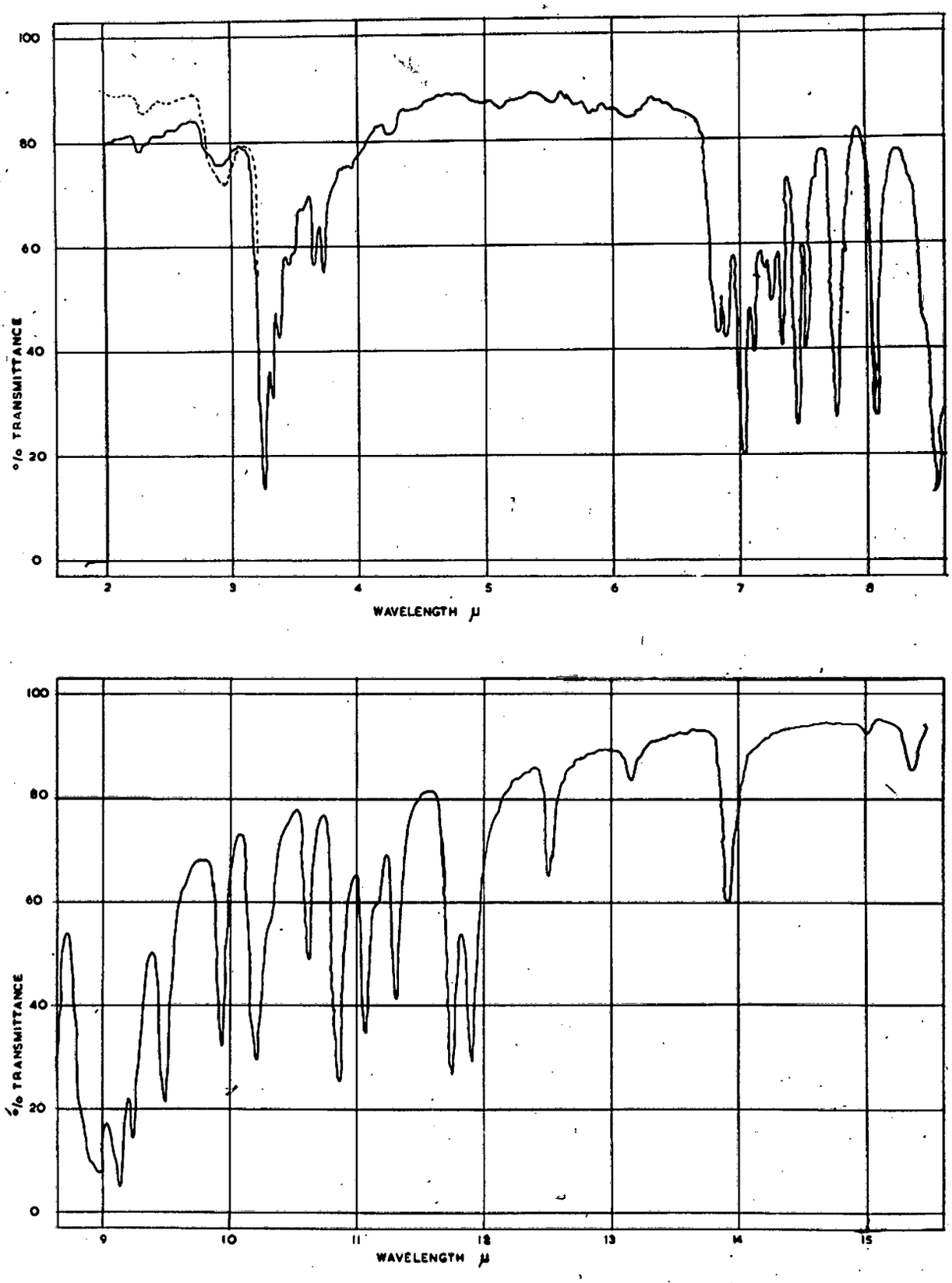


FIGURE VII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% TRANSMITTANCE
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The preparation of a sulphate of propaldazine was attempted by adding the azine, b.p. 144 - 146°C (0.46 g.; 1 mol.) in ether (5 ml.) to sulphuric acid (0.41 g.; 1 mol.) in an ethereal solution of approximately 2.5% w/v. A white precipitate resulted, which decomposed to the yellow azine and to proprionaldehyde as soon as the ether was removed by filtration. A fresh preparation, using slightly less than the theoretical quantity of sulphuric acid, gave a small yield of a white precipitate which was filtered rapidly, the last traces of ether being removed in a vacuum desiccator. (Found: N_2H_4, 17.3. $C_6H_{14}N_2SO_4$ requires N_2H_4, 15.2%). A repeated preparation yielded a further small sample containing 16.3% hydrazine. This substance decomposed so readily, and was obtained in such small quantity, that it was decided to try to make a complex salt of propaldazine, with the hope that such a salt might prove more stable. Hydrazine chlorostannate, dissolved in the minimum quantity of water, was treated with an excess of proprionaldehyde, and left at 50°C for several weeks, when ether was added. An oil which failed to crystallise separated out on further standing at -50°C.

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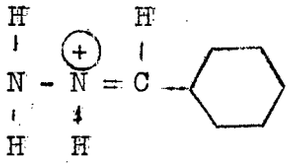

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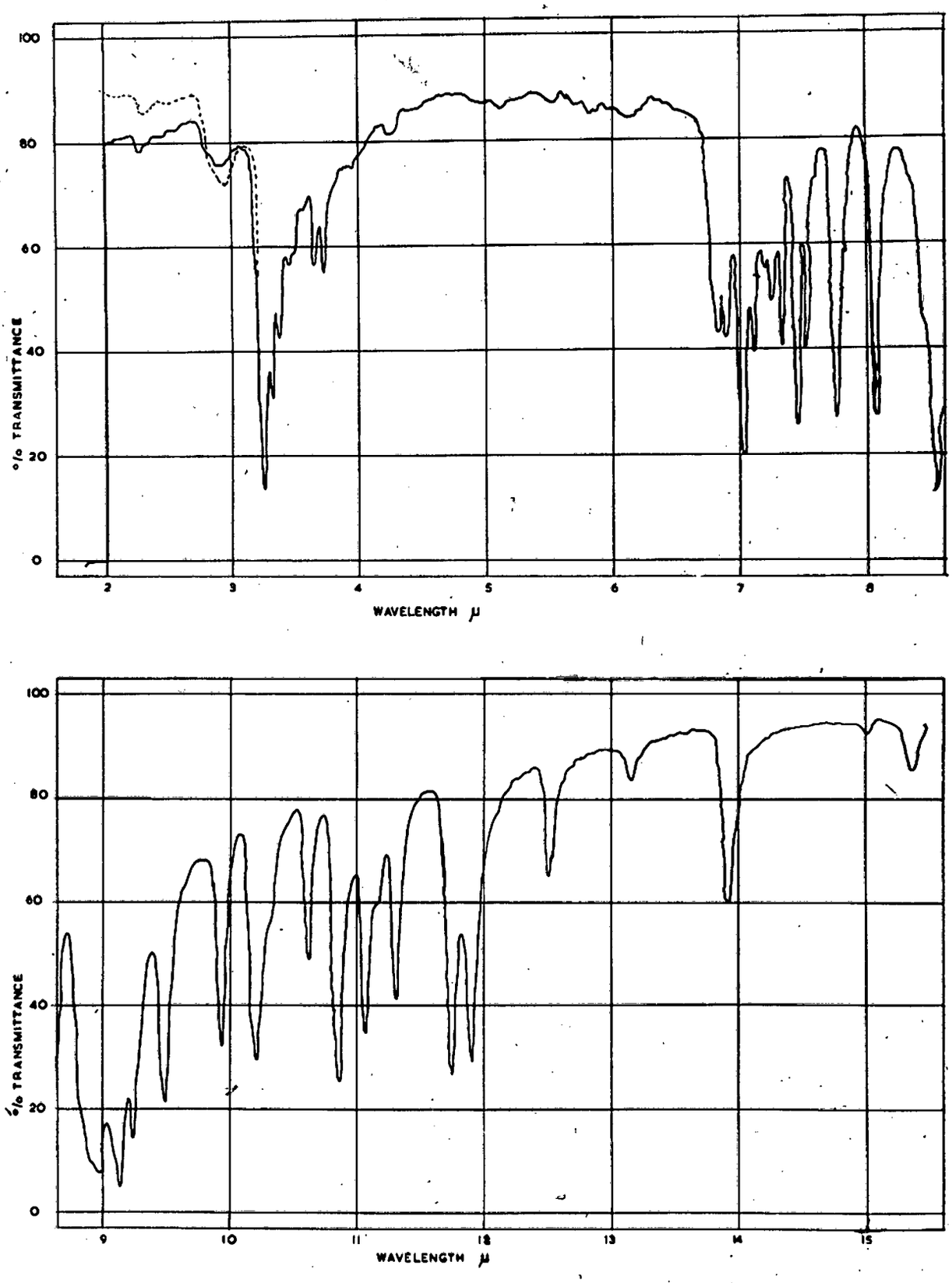
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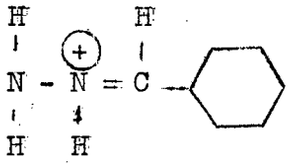

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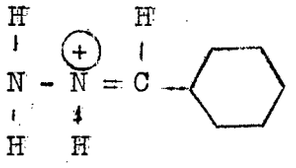

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The preparation of a sulphate of propaldazine was attempted by adding the azine, b.p. 144 - 146°C (0.46 g.; 1 mol.) in ether (5 ml.) to sulphuric acid (0.41 g.; 1 mol.) in an ethereal solution of approximately 2.5% w/v. A white precipitate resulted, which decomposed to the yellow azine and to proprionaldehyde as soon as the ether was removed by filtration. A fresh preparation, using slightly less than the theoretical quantity of sulphuric acid, gave a small yield of a white precipitate which was filtered rapidly, the last traces of ether being removed in a vacuum desiccator. (Found: N_2H_4, 17.3. $C_6H_{14}N_2SO_4$ requires N_2H_4, 15.2%). A repeated preparation yielded a further small sample containing 16.3% hydrazine. This substance decomposed so readily, and was obtained in such small quantity, that it was decided to try to make a complex salt of propaldazine, with the hope that such a salt might prove more stable. Hydrazine chlorostannate, dissolved in the minimum quantity of water, was treated with an excess of proprionaldehyde, and left at 50°C for several weeks, when ether was added. An oil which failed to crystallise separated out on further standing at -50°C.

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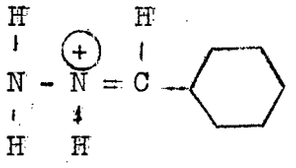

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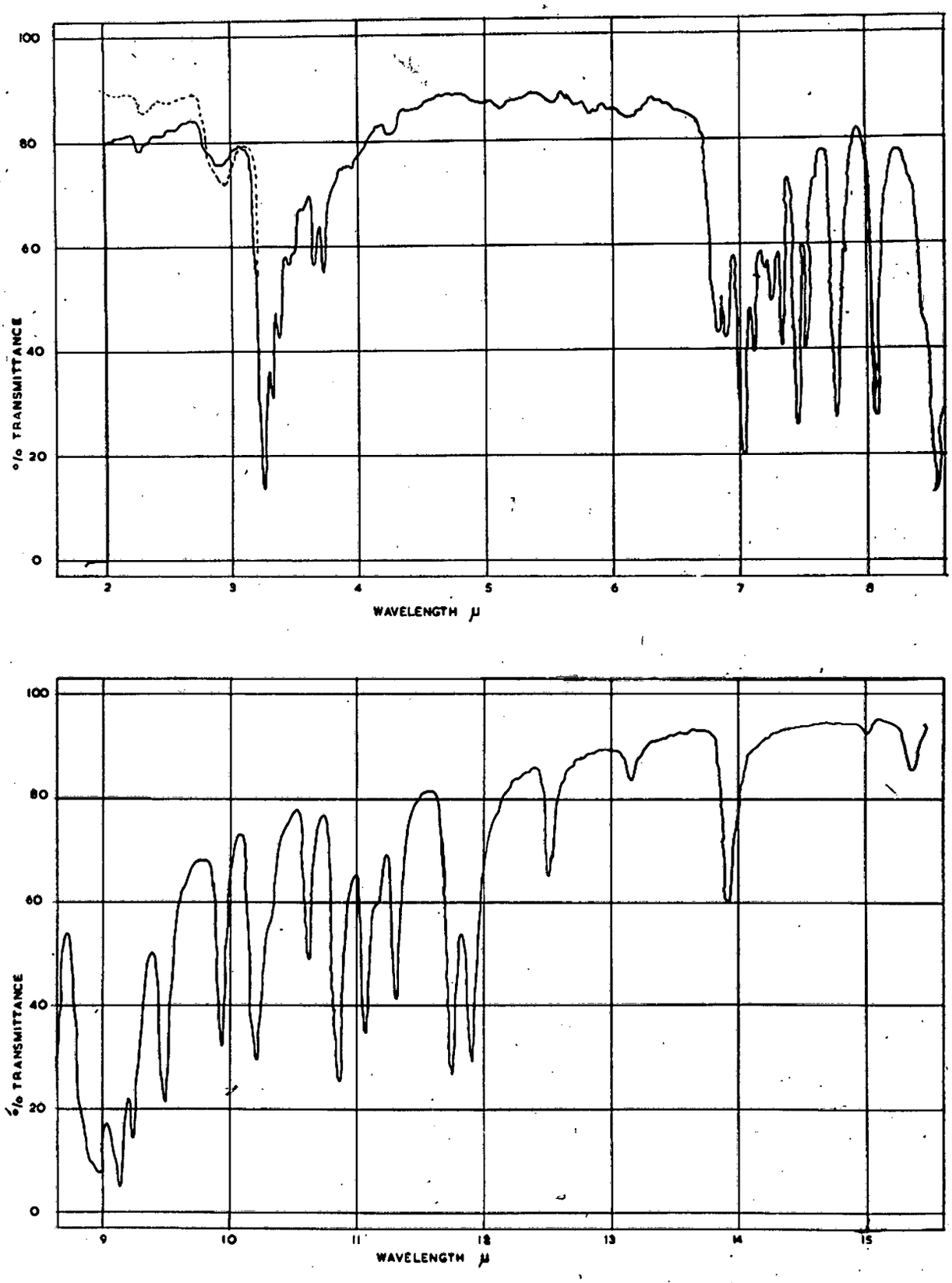
100
80
60
40
20
0
% TRANSMITTANCE
2
3
4
5
6
7
8
WAVELENGTH μ
100
80
60
40
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0
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9
10
11
12
13
14
15
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FIGURE X

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showed low chlorine and tin percentages for the chlorostannate, but a ratio Sn : Cl :: 1 : 6, indicating that the product was probably the chlorostannate of a polymerised base formed from crotonaldazine. This was confirmed by the hydrazine titration with iodate being extremely slow. As polycrmisation is known to occur in the presence of acids, another method of making the chlorostannate was tried, without the use of excessive quantities of acid. Thus a saturated aqueous solution of hydrazine chlorostannate was treated with crotonaldehyde. The solution became hot and a dark yellow-brown deposit formed. (Found: Cl, 16.1. $C_{16}H_{26}N_4SnCl_6$ requires Cl, 35.3%). This low figure for chlorine indicated that polymerisation had occurred, even under the above conditions, which supposition was confirmed by the slow liberation of crotonaldehyde and of hydrazine on acid hydrolysis. Repetition of the above yielded products of varying composition.

(b) <u>The structure of the polymerised product formed from acetaldehyde and hydrazine chlorostannate.</u>

The only preparation in which crystals of a definite and reproducible composition were obtained was in an attempt to make acetaldazine chlorostannate from hydrazine chlorostannate in saturated aqueous solution together with a large excess of acetaldehyde. On standing for several days at -50°C a small yield of white needles, which were shown to be a polymer of acetaldehyde, was obtained. On removing these, adding an equal volume of dry ether to the filtrate, and after standing several weeks at -50°C, large white crystals, m.p. 222.5 - 225°C, were formed. (Found: C, 33.6; H, 5.3; N_2H_4, 7.3 (approximately); Cl, 26.8; Sn, 14.9%). The hydrazine titration with iodate was very slow, the iodine being liberated over the course of two hours, the end point being indefinite. This indicated that a ring closed base had been formed, and hence the nitrogen content was determined by the Dumas combustion method. The empirical formula for the compound was shown by analysis to be $C_{22}H_{40-42}N_4O_6.SnCl_6$, which suggested that it was a chlorostannate of a base formed by the polymerisation of acetaldazine (probably

eleven molecules) together with hydrazine (two molecules). On heating with dilute sulphuric acid acetaldehyde was evolved, (characterised by its dinitrophenylhydrazone derivative). In order to try to elucidate the structure of this compound, in particular to try to find out the manner in which the oxygen in it was linked, its infra-red spectrum[18] (see Figure X) was examined. Due to the lack of a suitable solvent this was done by the potassium bromide pressed disc technique, 9.7 mg. of the compound in 1.00 g. potassium bromide being pressed to a disc of diameter one inch. As C = O groups normally absorb very strongly indeed at about 5.8μ, the lack of absorption in this region indicated a complete absence of such groups. Also the slight absorption at 6.1μ made the presence of C = C or C = N groups unlikely. Further, no -OH groups appeared to be present in the structure of the compound, as although there was slight absorption at 2.9μ, (which could have been due to -OH groups or to =NH stretching) this absorption decreased on leaving the potassium bromide disc in a desiccator over calcium chloride for twenty-four hours. Thus -OH groups, presumably in water, must have been present. That this was adsorbed water, and not water of crystallisation, was shown by heating the compound for two and a half hours at 100°C under reduced pressure, without loss in weight. It was therefore concluded that the oxygen atoms present in the structure must be linked as in ethers, possibly even in the cyclic form.

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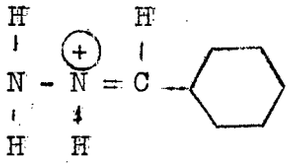

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An essential preliminary treatment for the removal of aldehyde was necessary before the aldazinium salts prepared below could be analysed completely. This was effected in two ways. All the simple and some of the complex salts were readily hydrolysed by acids with the evolution of the aldehyde. Thus 5N hydrochloric acid was used for the hydrolysis prior to a sulphate, hydrazine, bismuth or tin determination, and 2N sulphuric acid for a halogen or antimony estimation. The period of hydrolysis varied - the salts of benzaldazine being decomposed more rapidly than the corresponding ones of anisaldazine, whilst those of salicylaldazine were the most

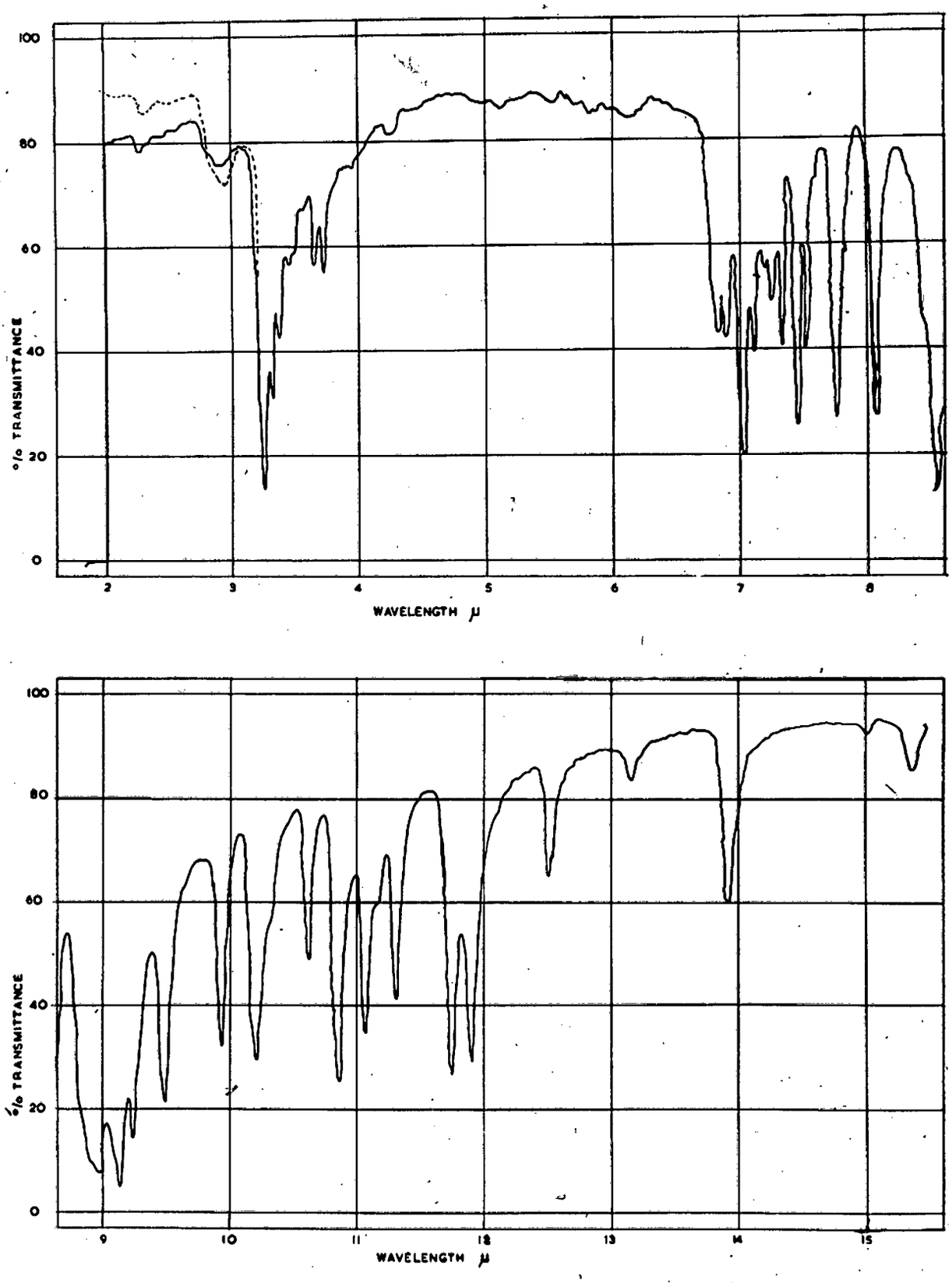
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FIGURE X

made to make its hydrochloride using the apparatus shown in Figure XII, page 37a, first working at room temperature, then at -50°C, as the oily products formed appeared to decompose readily, but no pure salt was isolated. Equally unsuccessful were all attempts at making the chlorostannate of n-butaldazine, both by mixing stoichiometric proportions of hydrazine chlorostannate, dissolved in the minimum of water, together with a large excess of butaldehyde followed by the addition of ether and retention at -50°C for a period of several months, and by working in completely anhydrous conditions in the apparatus shown in Figure XII, using butaldazine, pure stannic chloride and hydrogen chloride as starting materials.

The preparation of a sulphate of propaldazine was attempted by adding the azine, b.p. 144 - 146°C (0.46 g.; 1 mol.) in ether (5 ml.) to sulphuric acid (0.41 g.; 1 mol.) in an ethereal solution of approximately 2.5% w/v. A white precipitate resulted, which decomposed to the yellow azine and to proprionaldehyde as soon as the ether was removed by filtration. A fresh preparation, using slightly less than the theoretical quantity of sulphuric acid, gave a small yield of a white precipitate which was filtered rapidly, the last traces of ether being removed in a vacuum desiccator. (Found: N_2H_4, 17.3. $C_6H_{14}N_2SO_4$ requires N_2H_4, 15.2%). A repeated preparation yielded a further small sample containing 16.3% hydrazine. This substance decomposed so readily, and was obtained in such small quantity, that it was decided to try to make a complex salt of propaldazine, with the hope that such a salt might prove more stable. Hydrazine chlorostannate, dissolved in the minimum quantity of water, was treated with an excess of proprionaldehyde, and left at 50°C for several weeks, when ether was added. An oil which failed to crystallise separated out on further standing at -50°C.

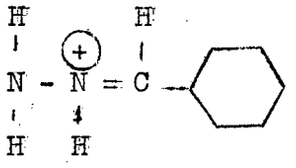
Next the preparation of salts of crotonaldazine was attempted. The preparation of the hydrochloride was tried by passing dry hydrogen chloride through an ethereal solution of crotonaldazine. A yellow brown precipitate formed immediately which on analysis

showed low chlorine and tin percentages for the chlorostannate, but a ratio Sn : Cl :: 1 : 6, indicating that the product was probably the chlorostannate of a polymerised base formed from crotonaldazine. This was confirmed by the hydrazine titration with iodate being extremely slow. As polycrmisation is known to occur in the presence of acids, another method of making the chlorostannate was tried, without the use of excessive quantities of acid. Thus a saturated aqueous solution of hydrazine chlorostannate was treated with crotonaldehyde. The solution became hot and a dark yellow-brown deposit formed. (Found: Cl, 16.1. $C_{16}H_{26}N_4SnCl_6$ requires Cl, 35.3%). This low figure for chlorine indicated that polymerisation had occurred, even under the above conditions, which supposition was confirmed by the slow liberation of crotonaldehyde and of hydrazine on acid hydrolysis. Repetition of the above yielded products of varying composition.

(b) <u>The structure of the polymerised product formed from acetaldehyde and hydrazine chlorostannate.</u>

The only preparation in which crystals of a definite and reproducible composition were obtained was in an attempt to make acetaldazine chlorostannate from hydrazine chlorostannate in saturated aqueous solution together with a large excess of acetaldehyde. On standing for several days at -50°C a small yield of white needles, which were shown to be a polymer of acetaldehyde, was obtained. On removing these, adding an equal volume of dry ether to the filtrate, and after standing several weeks at -50°C, large white crystals, m.p. 222.5 - 225°C, were formed. (Found: C, 33.6; H, 5.3; N_2H_4, 7.3 (approximately); Cl, 26.8; Sn, 14.9%). The hydrazine titration with iodate was very slow, the iodine being liberated over the course of two hours, the end point being indefinite. This indicated that a ring closed base had been formed, and hence the nitrogen content was determined by the Dumas combustion method. The empirical formula for the compound was shown by analysis to be $C_{22}H_{40-42}N_4O_6.SnCl_6$, which suggested that it was a chlorostannate of a base formed by the polymerisation of acetaldazine (probably

The hydrazone would now react with a solvated proton at the nitrogen atom having the higher electron density, i.e. at the nitrogen atom attached by the double bond to the carbon atom, forming V,



The final conversion of V to benzaldehyde and hydrazine would occur by a similar mechanism to that suggested above for the conversion of II to benzalhydrazone and benzaldehyde.

(4) Attempted preparations of aliphatic aldazinium salts.

(a) Attempted preparations of simple and complex salts of aliphatic azines.

, Attempts were made to prepare both simple and complex salts of acetaldazine, n-butaldazine, n-propaldazine and of crotonaldazine.

The preparation of a hydrochloride of acetaldazine was attempted by passing hydrogen chloride through its ethereal solution. This yielded a white crystalline product, consisting mainly of hydrazine dihydrochloride. All efforts to make the hydrohalides of this azine, if done in the presence of water, gave the corresponding hydrazinium salt. When working under strictly anhydrous conditions (using the apparatus shown in Figure XII, page 37a) oils which failed to crystallise even at -50°C were obtained.

Attempts to make a chloro- or bromo-stannate, a chloro-, bromo-, or iodo-antimonite of acetaldazine using different solvent and widely differing conditions, were equally unsuccessful. If done in the presence of even traces of water hydrazinium salts were precipitated, whereas when carried out in completely anhydrous conditions crystalline products were obtained which showed on analysis that the azine had polymerised in varying degrees.

n-Butaldazine, b.p. 186 - 188°C, was prepared and attempts were

III. EXPERIMENTAL.

(1) Preparations of aromatic aldazinium salts.

(a) Purity of reagents and solvents utilized.

The aromatic azines used as starting materials in the preparations of the series of salts, were made from hydrazine hydrate (60%; 1 mol.) and the stoichiometric quantity of aldehyde (2 mols.) in alcoholic solution. Benzaldazine[13], anisaldazine[14] and o-nitrobenzaldazine[12] were crystallised from ethanol, and salicylaldazine[13] from chloroform. The aliphatic azines, acetaldazine[15], n-propaldazine[16], n-butaldazine[16], and crotonaldazine[17] were prepared by the methods indicated in the references given.

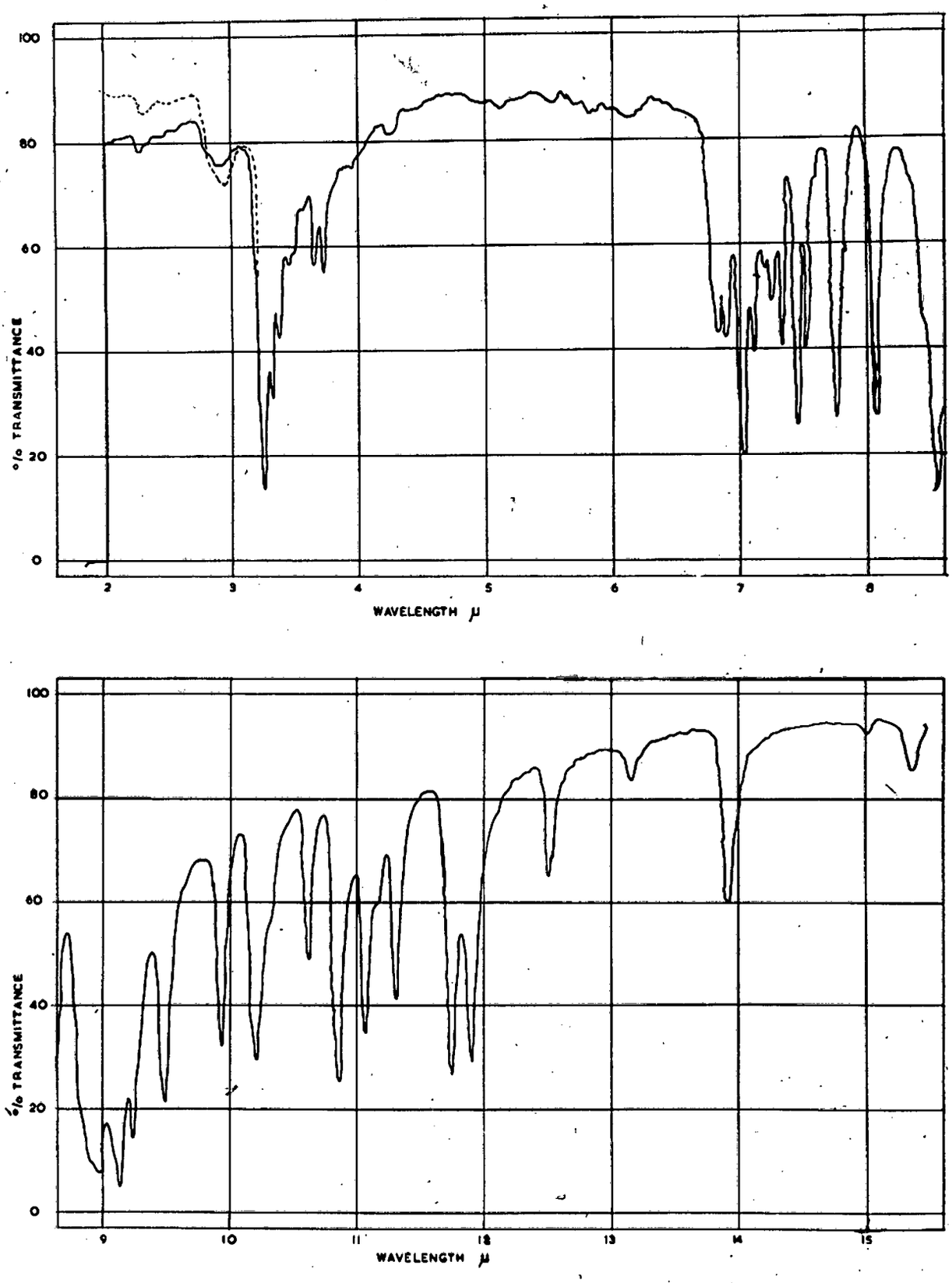
Hydrazine hexachlorostannate was prepared by fractional crystallisation of a mixture of stannic chloride pentahydrate and a saturated aqueous solution of hydrazine monohydrochloride.

The stannic chloride used for the various preparations had been purified by low pressure distillation, and was completely anhydrous, while the other metallic halides used were C.P. grade.

The solvents xylol, benzene and cyclohexane were dried by refluxing with sodium and were kept in containers with sodium wire, while the nitrobenzene was freshly distilled. The ether was distilled from concentrated sulphuric acid and also kept over sodium.

(b) Methods of analysis.

An essential preliminary treatment for the removal of aldehyde was necessary before the aldazinium salts prepared below could be analysed completely. This was effected in two ways. All the simple and some of the complex salts were readily hydrolysed by acids with the evolution of the aldehyde. Thus 5N hydrochloric acid was used for the hydrolysis prior to a sulphate, hydrazine, bismuth or tin determination, and 2N sulphuric acid for a halogen or antimony estimation. The period of hydrolysis varied - the salts of benzaldazine being decomposed more rapidly than the corresponding ones of anisaldazine, whilst those of salicylaldazine were the most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WAVELENGTH μ

FIGURE X

that the reaction was of the first order with respect to the azine concentration. The fact that at high acid concentrations (i.e. greater than 0.3 molar) the curve was no longer completely linear, did not necessarily mean a change in the order of the reaction, but was interpreted (see (a) above) as due to the formation of comparatively high concentrations of the hydrazone of benzaldehyde, the molecular extinctions of which would no longer be negligible. Similarly the shape of the log ε-time curve for the first twelve minutes of reaction was due to the presence of unchanged benzaldazine as well as of benzaldazinium ion.

The effect of different acid concentrations on the rate of the reaction was determined by measuring the rates at different molarities of hydrogen chloride, keeping the azine and the water concentrations the same. In order to obtain the specific velocity constants for the hydrolysis at various acid concentrations, the slopes of the corresponding log ε-time curves were required. Accordingly the curves shown in Figure IX were drawn. These represented the log ε against time curves for solutions of fixed azine concentration, but varying acid concentrations at the wave length of 295 mμ. This choice of wave length out of the five possible ones of 280, 285, 290, 295 and 300 mμ was made, as at the first three mentioned the absorption of the hydrazone of benzaldehyde formed affected the slopes of the log ε-time curves at the higher acid concentrations to a greater extent than at the last two wave lengths. Further 300 mμ was cut out as at this wave length the values of log ε dropped too low after a comparatively short time to fall on the more accurate part of the Beckmann spectrophotometeric scale. An examination of Figure IX showed that only on 0.48, 0.54 and 0.682 molar hydrogen chloride solutions did the log ε-time curves cease to be linear after about eighteen minutes. The specific velocity constants K, were obtained from the linear portions of the curves in Figure IX, from the relationship:-

$$K = \frac{-2.303}{\text{rate of change of log } \varepsilon \text{ with time}} \ \text{min}^{-1}$$

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stable to hydrolysis of all. The simple salts decomposed more rapidly than the complex ones. The complex chloro-salts were less stable than the corresponding bromo- which in turn were more stable than the iodo. The second method for the initial removal of aldehyde could be used prior to all determinations excepting that of hydrazine, as the aldehyde was removed partly as such and partly as unchanged azine. This method consisted in treating the salt with halogen free sodium hydroxide and acetone, and in then removing the aldehyde or azine by ether extraction in the case of benzaldazine, and by filtration after acidification in the case of anisaldazine and of salicylaldazine, these being insoluble in ether. This method had to be employed both for the analyses of those complex salts which were comparatively stable to dilute acid hydrolysis (namely for the bromostannates, the bromo-antimonites, and the bromobismuthites), and for those which were incompletely decomposed even by strong acid hydrolysis (namely the iodobismuthites).

After the preliminary removal of aldehyde by the first method, hydrazine was determined by an iodate titration (Andrew's Method). In the case of the three iodobismuthites the hydrazine was estimated by a Dumas nitrogen determination, owing to the extreme stability of these salts to acid hydrolysis. Halides were determined by Volhard's volumetric method, and sulphates gravimetrically as barium sulphate. Tin was separated as the sulphide then precipitated as the hydroxide,and determined gravimetrically as tin oxide. This method was found necessary as the shorter method of direct oxidation with concentrated nitric acid gave consistently low results. Bismuth was determined gravimetrically as the oxyhalide. Antimony was first separated as the sulphide (a double precipitation being necessary to separate traces of adsorbed halide) then dissolved in 50% (v/v) hydrochloric acid, boiled to remove all the hydrogen sulphide, diluted to the correct acid strength and titrated with iodate. Benzaldehyde was determined gravimetrically as the 2:4 dinitro-phentlhydrazone, after acid hydrolysis under reflux, in the presence

hydroxide recommended by Rice, Keller and Kirschner, as it could be applied with a brush and left a yellow mark which did not fade. At the first attempt no 2:4 dinitrophenylhydrazone of acetone was detected in the mixture. Accordingly the precipitation of these hydrazones was repeated removing the first crop obtained (which by m.p. was shown to be the 2:4 dinitrophenylhydrazone of benzaldehyde, which is much less soluble than the corresponding acetone compound). To the filtrate was added a furhter quantity of precipitating reagent, and the product formed was used successfully in the above chromatographic separation. The spot due to the acetone derivative travelled at a much faster rate than that of the other, showing clearly the presence of the acetone.

(d) Description of apparati used in preparations requiring anhydrous conditions.

The apparatus shown in Figure XI, was designed to allow of the precipitation of a salt by the passage of a current of dry hydrogen chloride, with the subsequent filtration and washing of the precipitate in situ; the whole process to be carried out under anhydrous conditions.

The salient features of the apparatus were a sintered glass filter tube fitted through a rubber bung to reach to the bottom of a reaction vessel, which was also connected to a dropping funnel through which precipitating agents and wash liquids could be added. A third inlet to the reaction vessel was connected through a two way tap to a source of dry air, and through a drying tube to a water pump. The filter tube was connected through a two-way tap to a source of dry hydrogen chloride and through a drying train to suction. The hydrogen chloride was generated in a Kipps' apparatus from ammonium chloride and concentrated hydrochloric acid, and was dried by passage through three wash bottles containing concentrated sulphuric acid. The air was dried by passage over calcium chloride, potassium hydroxide pellets and finally over phosphorus pentoxide. The rate of flow was controlled by passage through a wash bottle containing concentrated

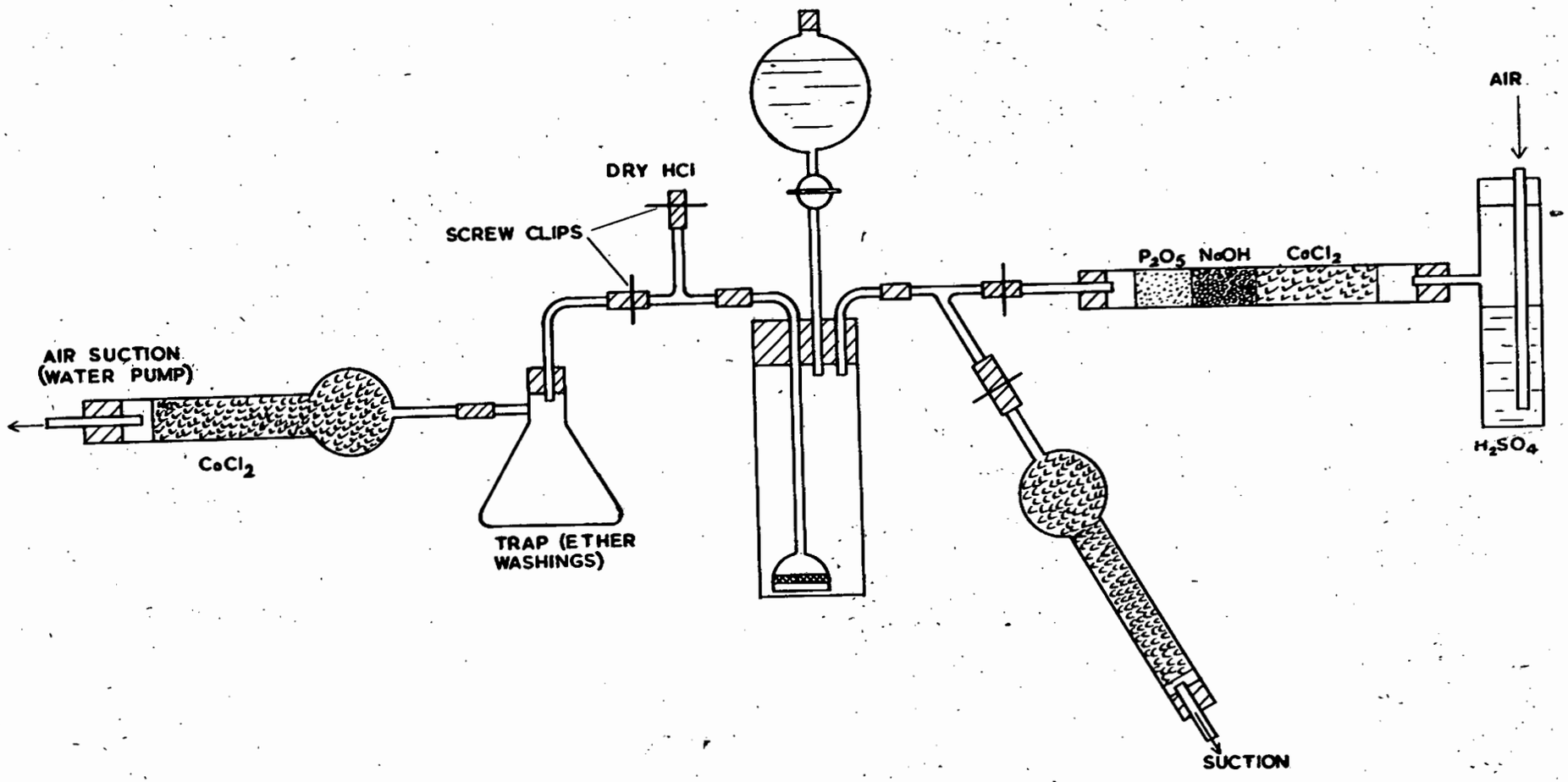

AIR
DRY HCl
SCREW CLIPS
P_2O_5 NaOH $CoCl_2$
AIR SUCTION (WATER PUMP)
$CoCl_2$
TRAP (ETHER WASHINGS)
H_2SO_4
SUCTION

FIGURE XI

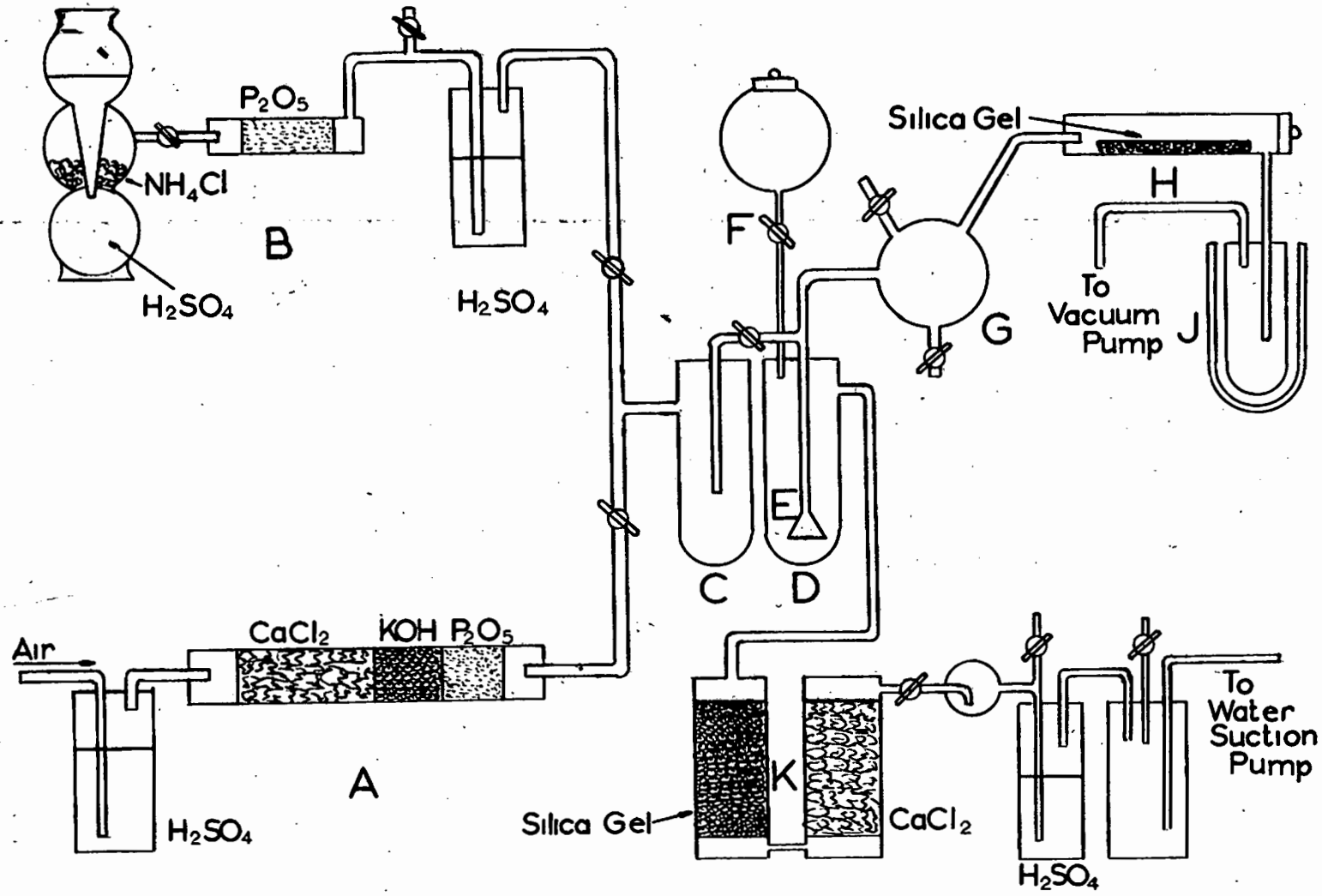
sulphuric acid.

During the process of precipitation it was found necessary to apply suction while passing the hydrogen chloride through the filter tube, in order to prevent clogging of the filter pad.

The apparatus shown in Figure XII was assembled when that previously used (shown in Figure XI) was found to be unsuitable for the preparations of salts of aliphatic azines. It was considered possible that a train which could exclude moisture entirely, might be more successful, and hence the second apparatus was designed, eliminating the use of rubber bungs.

It consisted of a train, A, to dry air entering the apparatus at various stages of the preparation, and of a Kipps' hydrogen chloride generator and drying train, B. Both of these trains led through taps into a vessel, C, fitted to the train by means of a ground glass joint. This vessel contained the solvent for washing the filter plate after the reaction was complete. Vessel, C, was joined by a glass tube to reaction vessel, D, through a filter plate, E. This vessel had sealed to it a separating funnel, F, used for introducing either starting materials or wash liquids, and an outlet tube which connected it to another drying train, K, and thence to a water suction pump. This pump was used to pull air or vapour through the apparatus. Through the stem of the filter tube was a lead to a separating funnel, G, into which the filtrate could be sucked. The separating funnel was connected to a tube, H, (with ground glass end containing a glass boat) which held drying agents. This in turn led to a liquid oxygen trap, J, and finally to a vacuum pump.

The air inlets on either side of the sulphuric acid wash bottle in the drying train, and the splash bulb between the sulphuric acid wash bottle and the calcium chloride tower in the same drying train, were found necessary to avoid the sulphuric acid sucking back on sudden alteration in pressure.


P_2O_5
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B
H_2SO_4
H_2SO_4
F
Silica Gel
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G
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J
E
C
D
Air
$CaCl_2$
KOH
P_2O_5
A
H_2SO_4
Silica Gel
K
$CaCl_2$
H_2SO_4
To Water Suction Pump

FIGURE XII

(e) Details of preparations of aromatic aldazinium salts.

The preparations described in this section are those of some hydrogen halides and hydrogen sulphates of aromatic aldazines, and of four hydrogen halides of "mixed" azines.

N:N'-Dibenzylidenehydrazinium Hydrogen Sulphate (benzaldazine hydrogen sulphate).

After investigating various solvents ether was found most satisfactory. Accordingly a solution of pure concentrated sulphuric acid in dry ether (2.5% strength w/v) was prepared. To benzaldazine (0.55 g.; 1 mol.) in dry ether (15 ml.) was added the stoichiometric quantity of the ether-sulphuric acid solution. Although the weight of sulphuric acid for a normal sulphate was taken the acid sulphate was precipitated, about half the expected weight being deposited. On adding a further quantity of ether-sulphuric acid solution (equal in volume to the first amount added) to the filtrate a further crop of acid sulphate was precipitated, (total yield 88%). On analysis the two crops were found to be the same, namely benzaldazine hydrogen sulphate, m.p. 160 - 161 C. (Found: C, 53.4; H, 4.4; N_2H_4, 10.5; SO_4, 31.7; C_7H_6O, 68. $C_{14}H_{13}N_2HSO_4$ requires C, 54.8; H, 4.6; N_2H_4, 10.5; SO_4, 31.4; C_7H_6O, 69%). This salt was found to be extremely hygroscopic.

No other sulphate of benzaldazine was prepared in a pure state, even after many attempts with different proportions of starting materials.

N:N'-Di-o-hydroxybenzylidenehydrazinium Bromide (Salicylaldazine hydrobromide).

This salt was made by floating a hot saturated solution of salicylaldazine in nitrobenzene (15 ml.) on a layer of 48% hydrobromic acid (5 ml.). The first crop of yellow crystals, separating at the interface were found to be contaminated with some hydrazine hydrobromide; the second crop, m.p. 211 - 213°C, was found to be salicylaldazine hydrobromide, (yield 20%). (Found: C, 50.9; H, 4.3; N_2H_4, 9.9; Br, 24.9. $C_{14}H_{13}N_2O_2Br$ requires C, 52.3; H, 4.1; N_2H_4, 10.0; Br, 24.9%).

N:N'-Di-o-hydroxybenzylidenehydrazinium Hydrogen Sulphate (salicylaldazine hydrogen sulphate).

The solvents chloroform, nitrobenzene and xylene were tried both for the azine and for the concentrated sulphuric acid, but were found to yield products contaminated with varying amounts of unchanged azine. Finally salicylaldazine (1.0 g.; 1 mol.) in dry xylene (50 ml.) was treated with the stoichiometric quantity of sulphuric acid (1 mol.) (in ethereal solution), in the apparatus shown in diagram A, and salicylaldazine hydrogen sulphate, m.p. 212 - 220°C, was precipitated in 70% yield. This salt was found to decompose to some extent when dried at 100°C under vacuum. (Found: C, 49.7; H, 4.4; N_2H_4, 9.5; SO_4, 28.3. $C_{14}H_{13}N_2O_2HSO_4$ requires C, 49.7; H, 4.2; N_2H_4, 9.5; SO_4, 28.4%).

N:N'Di-p-methoxybenzylidenehydrazinium Hydrogen sulphate (anisaldazine hydrogen sulphate).

When anisaldazine (0.5 g.; 1 mol.) dissolved in dry ether (10 ml.) was treated with the stoichiometric quantity of a 3.5% solution of sulphuric acid (98%) in dry ether, a yellow, crystalline powder of anisaldazine hydrogen sulphate, m.p. 202 - 203°C, was precipitated in 90% yield. (Found: C, 52.1; H, 8.7; N_2H_4, 8.7; SO_4, 26.3. $C_{16}H_{17}N_2O_2HSO_4$ requires C, 52.5; H, 8.7; N_2H_4, 8.7; SO_4, 26.2%).

N-Benzylidene-N'-isopropylidenehydrazinium Bromide.

After attempting to use benzaldazine, acetone and 48% hydrobromic acid as starting materials for making the above named salt and obtaining a mixture, another preparation was done adding benzaldehyde (2 ml.; 2 mols.) to 60% hydrazine hydrate (1.66 ml.; 1 mol.) in acetone (10 ml.) acidified with 48% hydrogen bromide. After heating, then cooling, white leaflets of the above name salt which were found to be contaminated with some benzaldazine hydrobromide separated. A further crop which was precipitated overnight yielded N-benzylidene-N'-isopropylidenehydrazinium bromide, m.p. 135 - 136°C,

after washing with boiling acetone until further washing did not alter the analysis, (total yield 55%). (Found: C, 49.6; H, 5.8; N_2H_4, 13.2; Br, 33.2. $C_{10}H_{13}N_2Br$ requires C, 49.8; H, 5.4; N_2H_4, 13.3; Br, 33.2%).

N-o-Hydroxybenzylidenehydrazinium-N'-isopropylidene Bromide.

This salt was prepared in three ways:-

(i) by boiling salicylaldazine (1 g.) with acetone (20 ml.) containing 48% hydrobromic acid (3 ml.);

(ii) by boiling acetone (20 ml.) with salicylaldehyde (1.5 ml.; 2 mols.), 60% hydrazine hydrate (0.6 ml.; 1 mol.), and 48% hydrobromic acid (0.4 ml.; 1 mol.);

(iii) by boiling the complex bromoantimonite of salicylaldazine (see page 47) with acetone.

The N-o-hydroxybenzylidenehydrazinium-N'-iso-propylidene Bromide crystallised on cooling the above solutions, in pink leaflets contaminated with traces of free salicylaldazine, which were removed with boiling acetone, in which the salt, m.p. 177 - 178°C, was found to be only sparingly soluble. (Found: C, 46.8; H, 5.0; N_2H_4, 12.5; Br, 31.2. $C_{10}H_{13}O_2NBr$ requires C, 46.7; H, 5.4; N_2H_4, 12.5; Br, 31.1%).

N-Benzylidene-N'-isopropylidenehydrazinium Iodide.

Attempts to make the above named salt from benzaldehyde and 60% hydrazine hydrate in acetone acidified with hydriodic acid were unsuccessful. It was prepared (in less than 5% yield) from dimethylketazine in benzaldehyde solution, acidified with 57% hydriodic acid. However, a better method of preparation was found to be as follows:- Benzaldazine (0.5 g.) dissolved in acetone (5 ml.), and cooled in ice, was mixed with 57% hydriodic acid (3 ml.) in acetone (2 ml.) also well cooled in ice. On standing in a closed vessel at 0°C, clusters of large, yellow crystals of the monohydrate of N-benzylidene-N'-isopropylidenehydrazinium iodide, m.p. 107 - 108°C, were formed in 60% yield. (Found: C, 38.8; H, 4.9; N_2H_4, 10.3;

I, 41.3; H_2O, 5.5. $C_{10}H_{13}N_2I,H_2O$ requires C, 39.2; H, 4.9; N_2H_4, 10.5; I, 41.5; H_2O, 5.9%). On heating at 56° under reduced pressure, it lost its water of hydration only. (Found, on anhydrous material: N_2H_4, 10.9; I, 44.4. $C_{10}H_{13}N_2I$ requires N_2H_4, 11.1; I, 44.1%).

On standing in air and more quickly in a desiccator, there was a slow loss of crystalline form, accompanied by a colour change from pale yellow, through orange to a red. This change was probably due to the loss of the water of hydration. After four months in a desiccator the iodide content of one sample changed from 41.3 to 42.8%, indicating partial loss of the water of hydration.

N-o-Nitrobenzylidene-N'-isopropylidenehydrazinium Bromide.

This salt separated in 60% yield as creamy white crystals, darkening with age, m.p. 156 - 158°, when 48% hydrobromic acid was added to o-nitrobenzaldehyde hydrazone in acetone. (Found: C, 41.9; H, 3.8; N_2H_4, 11.0; Br, 27.6. $C_{10}H_{12}O_2N_3Br$ requires C, 42.0; H, 4.2; N_2H_4, 11.0; Br, 27.4%).

(f) Details of the preparations of complex salts of aromatic aldazines.

The preparations described in this section are those of the halogeno-stannates, -antimonites and bismuthites of benzaldazine, salicylaldazine and anisaldazine, and of the chlorostannate of o-nitrobenzaldazine. A co-ordination compound of stannic chloride and salicylaldazine is also described.

Bis-(N:N'-dibenzylidenehydrazinium) Hexachlorostannate (benzaldazine chlorostannate).

Unsuccessful attempts were made to prepare the above salt by methods analogous to that used by Pugh and Stephen[2] for the preparation of acetone ketazine chlorostannate, starting with benzaldehyde, stannic chloride pentahydrate and hydrazine dihydrochloride in various solvents. Further attempts, using hydrazine chlorostannate and benzaldehyde, were equally unsuccessful.

Cl, 26.5; Sn, 15.0. $(C_{14}H_{13}O_2N_2)_2SnCl_6$ requires C, 41.4; H, 3.2; N_2H_4, 7.9; Cl, 26.2; Sn, 14.7%).

Bis-(N:N'-di-p-methoxybenzylidenehydrazinium) Hexachlorostannate. (Anisaldazine chlorostannate).

An attempt to prepare this salt from anisaldazine, stannic chloride and hydrogen chloride gas using xylene as solvent, yielded an impure product. Finally anisaldazine hydrochloride[2] (1.1 g.; 2 mols.) in nitrobenzene (10 ml.) was added to stannic chloride (0.5; 1 mol.) also in nitrobenzene (10 ml.). The yellow product obtained in 75% yield proved to be the required anisaldazine chlorostannate contaminated with a small amount of anisaldazine. Accordingly it was washed repeatedly with hot nitrobenzene, hot xylene and finally ether, until further washing did not alter the analyses. (Found: C, 44.2; H, 4.0; N_2H_4, 7.3; Cl, 24.2; Sn, 13.8. Calc. for $(C_{16}H_{17}O_2N_2)_2SnCl_6$ C, 44.2; H, 4.1; N_2H_4, 7.4; Cl, 24.5; Sn, 13.7%).

Bis-(N-N'-di-o-nitrobenzylidenehydrazinium) Hexachlorostannate (o-nitrobenzaldazine chlorostannate).

After attempts with various solvents had yielded impure products, the following method for preparing the above compound was evolved. Dry hydrogen chloride was passed through a mixture of stannic chloride (0.83 g.; 1 mol.) in nitrobenzene (20 ml.) and o-nitrobenzaldazine, m.p. 182°C, (1.90 g.; 2 mols.) in hot, dry xylol (30 ml.), and a greyish crystalline powder, m.p. 183 - 190° (blackening at 180°) of o-nitrobenzaldazine chlorostannate was precipitated in 55% yield. (Found: C, 37.0; H, 3.0; N_2H_4, 6.7; Cl, 22.7; Sn, 12.8. $(C_{14}H_{10}O_4N_4)_2SnCl_6$ requires C, 36.2; H, 2.4; N_2H_4, 6.9; Cl, 22.9; Sn, 12.8%).

Bis-(N-N'-dibenzylidenehydrazinium) Hexabromostannate (benzaldazine bromostannate).

Benzaldazine (2.1 g.; 2 mols.) in nitrobenzene (20 ml.) was added to stannic bromide (made from tin (0.61 g.; 1 mol.) and liquid bromine) in 47% hydrobromic acid (3 ml.). Two crops of yellow crystals (yield, 40%) of benzaldazine bromostannate, m.p.

240 - 242° were obtained, the first at the liquid interface, the second from the filtrate combined with nitrobenzene and ether washings. (Found: C, 32.4; H, 2.6; N_2H_4, 6.3; Br, 46.7; Sn, 11.6. $(C_{14}H_{13}N_2)_2SnBr_6$ requires C, 33.1; H, 2.6; N_2H_4, 6.3; Br, 47.2; Sn, 11.6%).

Bis-(N:N'-di-p-methoxybenzylidenehydrazinium) Hexabromostannate (anisaldazine hexabromostannate).

Anisaldazine (1.1 g.; 2 mols.) in nitrobenzene (10 ml.) was added to stannic bromide (made from tin (0.24 g.; 1 mol.) and liquid bromine) in 47% hydrobromic acid (3 ml.). Two crops of a yellow, crystalline product were obtained (yield, 90%), the first from the liquid interface, the second from the filtrate combined with nitrobenzene and ether washings. Analysis indicated that the products were contaminated with small amounts of anisaldazine, but washing either crop with hot nitrobenzene and finally with ether, afforded anisaldazine hexabromostannate as a yellow crystalline powder, m.p. 240 - 242°. (Found: C, 33.9; H, 2.9; N_2H_4, 5.6; Br, 42.2; Sn, 10.5; $(C_{16}H_{16}O_2N_2)_2SnBr_6$ requires C, 34.3; H, 3.0; N_2H_4, 5.6; Br, 42.3; Sn, 10.4%).

N:N'-Dibenzylidenehydrazinium Tetrachloroantimonite (benzaldazine chloroantimonite).

Dry hydrogen chloride was passed through anhydrous antimony trichloride (1.48 g.; 1 mol.) in nitrobenzene (10 ml.) mixed with benzaldazine (1.35 g.; 1 mol.) in the same solvent (20 ml.). Pale yellow crystals of benzaldazine chloroantimonite, m.p. 156 - 157°C, were deposited, (yield, 90%). (Found: C, 35.2; H, 2.7; N_2H_4, 6.8; Sb, 26.1; Cl, 30.7. $C_{14}H_{13}N_2SbCl_4$ requires C, 35.5; H, 2.7; N_2H_4, 6.8; Sb, 25.8; Cl, 30.2%).

N:N'-di-o-hydroxybenzylidenehydrazinium Tetrachloroantimonite (salicylaldazine chloroantimonite).

Dry hydrogen chloride was passed through a mixture of antimony trichloride (1.32 g.; 1 mol.) in nitrobenzene (10 ml.) and salicylaldazine (1.39 g.; 1 mol.) in nitrobenzene (20 ml.). Yellow crystals of salicylaldazine chloroantimonite, m.p. 175 - 182°C, were

were deposited, (yield, 97%). (Found: C, 33.7; H, 2.5; N_2H_4, 6.2; Cl, 28.1; Sb, 24.1. $C_{14}H_{13}O_2N_2SbCl_4$ requires C, 33.3; H, 2.6; N_2H_4, 6.3; Cl, 28.1; Sb, 24.2%).

N:N'-di-p-methoxybenzylidenehydrazinium Tetrachloroantimonite (anisaldazine chloroantimonite).

Dry hydrogen chloride was passed through a mixture in nitrobenzene (20 ml.) of anhydrous antimony trichloride (0.68 g.; 1 mol.) and anisaldazine (0.80 g.; 1 mol.), and the orange-yellow crystals of anisaldazine chloroantimonite, m.p. 198 - 200°C, (yield 80%) which formed were collected and washed with nitrobenzene and finally ether. (Found: C, 36.1; H, 3.5; N_2H_4, 6.2; Sb, 22.9; Cl, 26.5. $C_{16}H_{17}O_2N_2SbCl_4$ requires C, 36.0; H, 3.2; N_2H_4, 6.0; Sb, 22.9; Cl, 26.7%).

N:N'-Dibenzylidenehydrazinium Tetrabromoantimonite (benzaldazine bromoantimonite).

The first attempt to prepare the above salt from stoichiometric quantities of antimony tribromide, hydrazine hydrate, 47% hydrobromic acid and benzaldehyde in absolute ethanol gave as a product yellow granular crystals of undecahydrazinium heptadecaiododiantimonite. (Found: N_2H_4, 18.2; Sb, 12.5; Br, 69.8. $(N_2H_5)_{11}Sb_2Br_{17}$ requires N_2H_4, 18.3; Sb, 12.4; Br, 69.2%).

Several attempts to prepare the above named substance yielded a compound of constant composition and m.p. 183 - 187°C, which on analysis proved to have the empirical formula $C_{56}H_{52}N_8Sb_3Br_{13}$, being possibly a double salt of composition $3.SbBr_3.4(C_{14}H_{13}N_2Br)$. This substance was formed when antimony trioxide (1 g.; 1 mol.) dissolved in 47% hydrobromic acid (3 ml.) was mixed with hydrazine hydrate (64%, 0.6 ml.; 1 mol.) and benzaldehyde (1.4 ml.; 4 mols.) added dropwise with shaking. The whole was heated to boiling, and on cooling an orange-yellow powder having the above composition separated. On crystallising from ethanol clusters of orange crystals having the same melting point and composition were obtained. (Found: C, 30.6; H, 2.4; N_2H_4, 5.5; Sb, 15.8; Br, 45.3. $(C_{14}H_{13}N_2)_4Sb_3Br_{13}$ requires C, 30.0; H, 2.3; N_2H_4, 5.7; Sb, 16.3; Br, 46.3%). Crystals of

the same shape, colour, m.p. and percentage composition separated overnight at the liquid interface on mixing benzaldazine (1.42 g.; 2 mols.) in nitrobenzene (20 ml.) with antimony trioxide (1 g.; 1 mol.) dissolved in 47% hydrobromic acid (3 ml.).

The second method described above was then repeated with the slight modification of omitting the heating, (as it was considered possible that some decomposition might have occurred during that stage of the preparation) and using dry ether to dissolve the benzaldehyde before its addition. Two crops of yellow crystals were obtained. The first, m.p. 141 - 147°C, appeared to be the desired compound contaminated with hydrazine hydrobromide, the second m.p. 176 - 178°C was the required benzaldazine bromoantimonite (yield, less than 5%). (Found: C, 25.9; H, 2.2; N_2H_4, 4.5; Sb, 18.6; Br, 50.0. $C_{14}H_{13}N_2SbBr_4$ requires C, 25.8; H, 2.0; N_2H_4, 4.9; Sb, 18.7; Br, 49.2%).

In order to obtain a better yield it was decided to repeat the preparation, using benzaldazine (0.69 g.; 1 mol.) in nitrobenzene (15 ml.) and anhydrous antimony tribromide (1.20 g.; 1 mol.) dissolved in 47% hydrobromic acid (3 ml.). The first crop of yellow crystals obtained were found to be impure. A second crop of crystals, which proved to be hydrazine hydrobromide, separated from the combined filtrate and washings. On standing overnight a third crop (yield 20%) was obtained; these consisted of pure benzaldazine bromoantimonite, m.p. 179 - 180°C. (Found: C, 25.9; H, 2.2; N_2H_4, 4.8; Sb, 18.7; Br, 49.4%). As the yield of this product was still low, it was decided to try to improve it. As it seemed evident that the benzaldazine bromoantimonite was not stable to heat, the second method of preparation was repeated, omitting the heating, and cooling the reaction mixture between the various additions of reagents. One crop of benzaldazine bromoantimonite, m.p. 176 - 177°C, was obtained in 40% yield. (Found: N_2H_4, 5.0; Sb, 18.4; Br, 49.2%).

N:N'-Di-o-hydroxybenzylidenehydrazinium Tetrabromoantimonite (salicylaldazine bromoantimonite).

Unsuccessful attempts to prepare the above compound were made starting with antimony trioxide, hydrazine hydrate, hydrobromic acid and salicylaldehyde as starting materials, although this method had been utilised in the preparation of the corresponding benzaldazine salt. The products obtained were invariably contaminated with salicylaldazine. Many extractions with hot solvents, in order to remove the unchanged azine, were unsuccessful in this purpose. One extraction with acetone caused the formation of pink leaflets which, on analysis, proved to be N-o-hydroxybenzylidene-N'-isopropylidene-hydrazinium bromide (see p. 40).

On using stoichiometric quantities of antimony tribromide and salicylaldazine both in nitrobenzene solution, together with a layer of 47% hydrobromic acid, a product was obtained which was contaminated with a small amount of salicylaldazine hydrobromide. The latter was removed partially, but not completely, by repeated extractions with hot nitrobenzene.

Finally a solution of salicylaldazine (1.65 g.; 2 mols.) in hot nitrobenzene (30 ml.) was added to antimony trioxide (1 g.; 1 mol.) dissolved in hot 47% hydrobromic acid (3 ml.). On standing, golden-yellow, crystalline plates, m.p. 192 - 193°C, of salicylaldazine bromoantimonite formed at the liquid interface. (Found: C, 24.7; H, 1.9; N_2H_4, 4.8; Sb, 17.9; Br, 47.0. $C_{14}H_{13}O_2N_2SbBr_4$ requires C, 24.6; H, 1.9; N_2H_4, 4.7; Sb, 17.9; Br, 46.9%). On repeating the above preparation two crops of crystals were obtained, the first being contaminated with some unchanged salicylaldazine, the second being the pure bromoantimonite.

N:N'-Di-p-methoxybenzylidenehydrazinium Tetrabromoantimonite (anisaldazine bromoantimonite).

A layer of 47% hydrobromic acid was added to anhydrous antimony tribromide (1.0 g.; 1 mol.) in nitrobenzene (8 ml.) mixed with anisaldazine (0.89 g.; 1 mol.) in nitrobenzene (12 ml.). Two

crops of yellow-orange crystals of anisaldazine bromoantimonite, m.p. 216 - 218°C, were obtained (yield, 80%), the first from the liquid interface, the second from the filtrate combined with nitrobenzene and ether washings. (Found: C, 27.6; H, 2.7; N_2H_4, 4.5; Sb, 17.1; Br, 45.0. $C_{16}H_{17}O_2N_2SbBr_4$ requires C, 27.0; H, 2.4; N_2H_4, 4.5; Sb, 17.2; Br, 45.1%).

N:N'-Dibenzylidenehydrazinium Tetraiodoantimonite (benzaldazine iodantimonite).

A quantity of antimony tri-iodide was prepared from iodine and powdered antimony; the purity being found by an iodate titration to be 99.0%.

Attempts to make the above compound from antimony tri-iodide (1 g.; 1 mol.), 60% hydrazine hydrate (0.2 ml., 1 mol.) acidified with 57% hydriodic acid and benzaldehyde (0.4 ml.; 2 mols.) in absolute ethanol as solvent yielded, after boiling and cooling, red, rhombic crystals of undecahydrazinium heptadecaiododiantimonite in 10% yield. (Found: N_2H_4, 12.8; Sb, 8.9; I, 78.9. $(N_2H_5)_{11}Sb_2I_{17}$ requires N_2H_4, 13.1; Sb, 8.8; I, 78.1%).

Further unsuccessful attempts to make benzaldazine iodoantimonite from antimony tri-iodide and benzaldazine, both in nitrobenzene and in xylene solutions, together with hydriodic acid, were made. Finally antimony tri-iodide (1 g.; 1 mol.) in 57% hydriodic acid (1 ml.) was heated in dry xylene (5 ml.), and benzaldazine (0.69 g.; 1 mol.) dissolved in ether (10 ml.) were added. A red-orange crystalline powder of benzaldazine iodoantimonite, m.p. 173 - 190°C, was precipitated in 70% yield. (Found: C, 20.8; H, 1.6; N_2H_4, 3.6; Sb, 15.0; I, 60.7. $C_{14}H_{13}N_2SbI_4$ requires C, 20.1; H, 1.5; N_2H_4, 3.8; Sb, 14.5; I, 60.5%).

N:N'-Di-o-hydroxybenzylidenehydrazinium Tetraiodoantimonite (salicylaldazine iodoantimonite).

The first few attempts to make the above compound yielded products contaminated with salicylaldazine. Accordingly the following method

state on passing hydrogen chloride through solutions of salicylaldazine in various solvents, the above named compound was made from salicylaldazine (1.2 g.; 1 mol.) in nitrobenzene (30 ml.) mixed with a solution of anhydrous bismuth chloride (1.58 g.; 1 mol.) in nitrobenzene (20 ml.) through which dry hydrogen chloride gas had been passed for ten minutes. After the mixing of the two solutions the passage of the gas was continued for a further fifteen minutes. Orange crystals of salicylaldazine chlorobismuthite, m.p. 213 - 220°C, formed in 87% yield. (Found: C, 28.0; H, 2.6; N_2H_4, 5.5; Cl, 24.3; Bi, 35.2. $C_{14}H_{13}N_2O_2BiCl_4$ requires C, 28.4; H, 2.2; N_2H_4, 5.4; Cl, 24.0; Bi, 35.3%).

N:N'-Di-p-methoxybenzylidenehydrazinium Tetrachlorobismuthite (anisaldazine tetrachlorobismuthite).

Anisaldazine hydrochloride[7], m.p. 162 - 166°C, (1.5 g.; 1 mol.) in nitrobenzene (25 ml.) was heated with anhydrous bismuth chloride (1.6 g.; 1 mol.) in nitrobenzene (20 ml.) and on cooling, orange crystals of anisaldazine chlorobismuthite, m.p. 236.5 - 237.5°C, separated in 80% yield. (Found C, 30.9; H, 3.1; N_2H_4, 5.2; Cl, 22.9; Br, 33.6. $C_{16}H_{17}O_2N_2BiCl_4$ requires C, 31.0; H, 2.7; N_2H_4, 5.2; Cl, 22.9; Bi, 33.7%).

N:N'-Dibenzylidenehydrazinium Tetrabromobismuthite (benzaldazine bromobismuthite).

Mixtures of the above named salt together with benzaldazine hydrobromide were obtained when using bismuth oxycarbonate in 47% hydrobromic acid, together with hydrazine hydrate and benzaldehyde either with or without ether as solvent.

Finally bismuth oxycarbonate (0.83 g.; 1 mol.) in 48% hydrobromic acid (4 ml.) together with benzaldazine (0.52 g.; 1 mol.) in nitrobenzene (15 ml.), deposited at the liquid interface pale yellow crystals of benzaldazine bromobismuthite, m.p. 229 - 234°C, in 70% yield. (Found: C, 22.4; H, 1.7; N_2H_4, 4.3; Br, 43.8; Bi, 27.7. $C_{14}H_{13}N_2BiBr_4$ requires C, 22.8; H, 1.8; N_2H_4, 4.3; Br, 43.4; Bi, 28.3%).

N:N'-Di-o-hydroxybenzylidenehydrazinium Tetrabromobismuthite (salicylaldazine bromobismuthite).

Many preparations of the above named salt were attempted using different starting materials and solvents, but the products obtained were contaminated with varying amounts of unchanged salicylaldazine.

Finally salicylaldazine (1.1 g.; 1 mol.) in nitrobenzene (50 ml.) was mixed with bismuth oxycarbonate (1.16 g.; 1 mol.) in 48% hydrobromic acid (5 ml.); the whole was heated, cooled and fractionally crystallised. The fourth crop of orange crystals, m.p. ca. 227°C, was shown by analysis to be comparatively pure salicylaldazine bromobismuthite in less than 5% yield. (Found: N_2H_4, 4.6; Br, 40.3. $C_{14}H_{13}O_2N_2BiBr_4$ requires N_2H_4, 4.2; Br 41.6%).

N:N'-Di-p-methoxybenzylidenehydrazinium Tetrabromobismuthite (anisaldazine bromobismuthite).

After attempted preparations with different solvents, xylene was found to yield the purest product. Bismuth oxycarbonate (1.16 g.; 1 mol.) dissolved in 48% hydrobromic acid (4 ml.) together with anisaldazine (1.33 g.; 1 mol.) in dry xylene (70 ml.), deposited yellow-orange crystals of anisaldazine bromobismuthite, (yield, 33%) contaminated with a small quantity of unchanged anisaldazine. After repeated washings with hot xylene, hot nitrobenzene and finally dry ether, the analysis and m.p. of 244.5 - 245.5°C remained unchanged. (Found: C, 25.3; H, 2.4; N_2H_4, 4.2; Br, 40.6; Bi, 26.2; $C_{16}H_{17}N_2O_2BiBr_4$ requires C, 24.3; H, 2.2; N_2H_4, 4.1; Br, 40.5; Bi, 26.2%).

N:N'-Dibenzylidenehydrazinium Tetraiodobismuthite (benzaldazine iodobismuthite).

Bismuth tri-iodide (0.80 g.; 1 mol.) in 57% hydriodic acid (3 ml.) was added to benzaldazine (0.28 g.; 1 mol.) in nitrobenzene (15 ml.), and on standing for two days large red crystals of benzaldazine iodobismuthite, m.p. 228 - 230°C, were deposited in 30% yield. (Found: C, 17.9; H, 1.7; N_2H_4, 3.8; I, 55.2; Bi; 22.4. $C_{14}H_{13}N_2BiI_4$ requires C, 18.2; H, 1.4; N_2H_4, 3.5; I, 54.8; Bi, 22.6%).

N:N'-Di-o-hydroxybenzylidenehydrazinium Tetraiodobismuthite (salicylaldazine iodobismuthite).

Bismuth tri-iodide (0.80 g.; 1 mol.) in 57% hydriodic acid (3 ml.) was added to salicylaldazine (0.33 g.; 1 mol.) in nitrobenzene (30 ml.) and after standing for ten days, large red crystals of salicylaldazine iodobismuthite, m.p. 246 - 253°C, were deposited in 15% yield. (Found: C, 17.4; H, 1.6; N_2H_4, 3.3; Bi, 21.6. $C_{14}H_{13}O_2N_2BiI_4$ requires C, 17.4; H, 1.4; N_2H_4, 3.3; Bi, 21.8%).

N:N'-Di-p-methoxybenzylidenehydrazinium Tetraiodobismuthite (anisaldazine tetraiodobismuthite).

Bismuth tri-iodide (0.80 g.; 1 mol.) in 57% hydriodic acid (3 ml.) was added to anisaldazine (0.35 g.; 1 mol.) in nitrobenzene (20 ml.), and overnight large, dark violet crystals of anisaldazine tetraiodobismuthite, m.p. 235 - 238°C, separated out in 70% yield. (Found: C, 19.6; H, 1.6; N_2H_4, 3.1; I, 51.0; Bi, 20.8. $C_{16}H_{17}O_2N_2BiI_4$ requires C, 19.5; H, 1.7; N_2H_4, 3.2; I, 51.5; Bi, 21.2%).

Co-ordination compound of 1 mol. stannic chloride and 2 mols. salicylaldazine.

Ether, chloroform, carbon tetrachloride, benzene, xylene and tetralene were all tried in turn as solvents for both salicylaldazine and for stannic chloride. Although tetralene was found to be the best solvent for the azine, it was found to react with stannic chloride. Finally xylene was chosen as the most suitable solvent.

The above addition compound, 1 mol. stannic chloride : 2 mols. salicylaldazine, was precipitated from a solution in xylene of 1 mol. stannic chloride : 1 mol. azine. Accordingly the preparation was repeated several times using the correct molecular proportions, i.e. stannic chloride (1.04 g.; 1 mol.) in xylene (10 ml.) was added to salicylaldazine (1.92 g.; 2 mols.) in xylene (45 ml.) with the exclusion of moist air. The above mentioned addition compound, m.p. 224 - 231°C, was precipitated in 86% yield. (Found: C, 46.9; H, 3.3; N_2H_4, 8.7; Cl, 19.0; Sn, 16.0. $C_{28}H_{24}N_4O_4SnCl_4$ requires C, 45.4; H, 3.2; N_2H_4, 8.6; Cl, 19.0; Sn, 16.0%).

(g) Attempted preparations of a hydrochloride of salicylaldazine.

Many unsuccessful attempts to prepare a hydrochloride of salicylaldazine in a pure state were made. Hydrogen chloride was passed through solutions of this azine in various solvents (chloroform cyclohexane, benzene, nitrobenzene and xylene) using the apparatus shown in Figure XI, page 36a. The products obtained were invariably found to be contaminated with some unchanged azine, which could not be extracted successfully with hot solvents, as this process also appeared to cause some decomposition of the chief product, presumably from the analysis figures, the desired hydrochloride.

Thus it appeared that it would be no use to attempt to make salicylaldazine hydrochloride using the azine as starting material owing to the three factors:-

(i) The azine was only soluble in hot solvents, whereas the hydrochloride, if it existed, would probably evolve hydrogen chloride in the hot, in the absence of water, as did benzaldazine hydrochloride.

(ii) When water was entirely excluded, and benzene used as solvent in the hot, the azine remained unchanged.

(iii) If moisture was present, even in traces, hydrolysis to hydrazine hydrochloride occurred readily, owing to the high temperature.

Hence it was decided to try to use hydrazine hydrochloride as starting material with salicylaldehyde. Accordingly secondary butyl alcohol, n-butyl alcohol and cyclohexane were tried as solvents. However, the hydrazine hydrochloride was only slightly soluble in these solvents, and when salicylaldehyde was added to the saturated solutions only a small quantity of salicylaldazine was precipitated. Finally methyl alcohol was used as solvent. After heating to dissolve the hydrazine dihydrochloride in methanol, an excess of salicylaldehyde was added. A pale cream precipitate of salicylaldazine (Found: Cl, nil; N_2H_4, 13.2%) resulted. This was repeated using theoretical quantities of starting materials (i.e. 1 mol. $N_2H_6Cl_2$ + 2 mols. salicylaldehyde) and on cooling large, pale-yellow crystals of salicylaldazine, contaminated with hydrazine dihydrochloride separated.

At this stage it was decided to abandon the preparation of

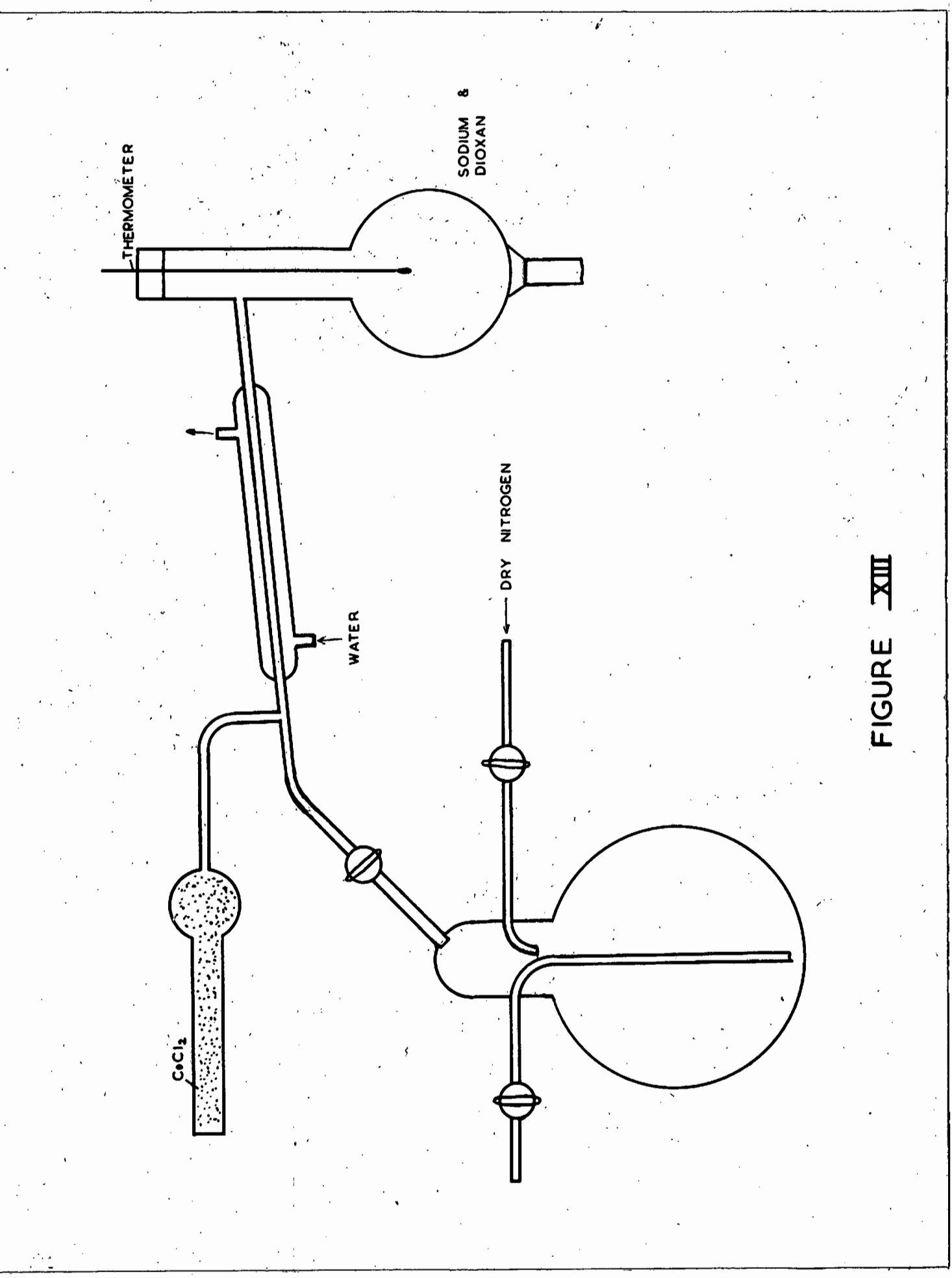

FIGURE XIII

salicylaldazine hydrochloride, as it seemed unlikely that a suitable solvent could be found for hydrazine hydrochloride, which would also dissolve the azine, but would precipitate its hydrochloride.

2. (a) Purification and storage of solvent, dioxan.

Three litres of dioxan were dried[15] by refluxing for forty-eight hours with metallic sodium, and were then distilled directly into a flask for storage under nitrogen in the dark, so that the solvent could be expelled by nitrogen pressure without the admission of moisture. (See Figure XIII). The absorption spectrum of a sample of this dioxan was determined (Figure XIV) and the solvent was found to transmit more than 90% of the light from a wave length of 280 mμ upwards. Between 275 mμ and 280 mμ the transmission was between 85% and 90%, which meant that readings in this wave length range would be obtainable, but might not be so accurate as those at higher wave lengths. (See Table I).

TABLE I.

Transmittance curve for purified dioxan.

Wave length in mμ	Transmitting %age
250	1.5
255	1.0
260	4.5
265	29.0
270	65.5
275	86.0
280	92.0
285	95.0
288	96.0
290	97.5
295	98.0
300	100.0
305	100.0
310	100.0
320	100.0
330	100.0
340	100.0
350	100.0

(b) Determination of the water content of the solvent, dioxan.

The water content of the solvent, dioxan, was determined by a standard Karl Fischer titration. The Karl Fischer reagent

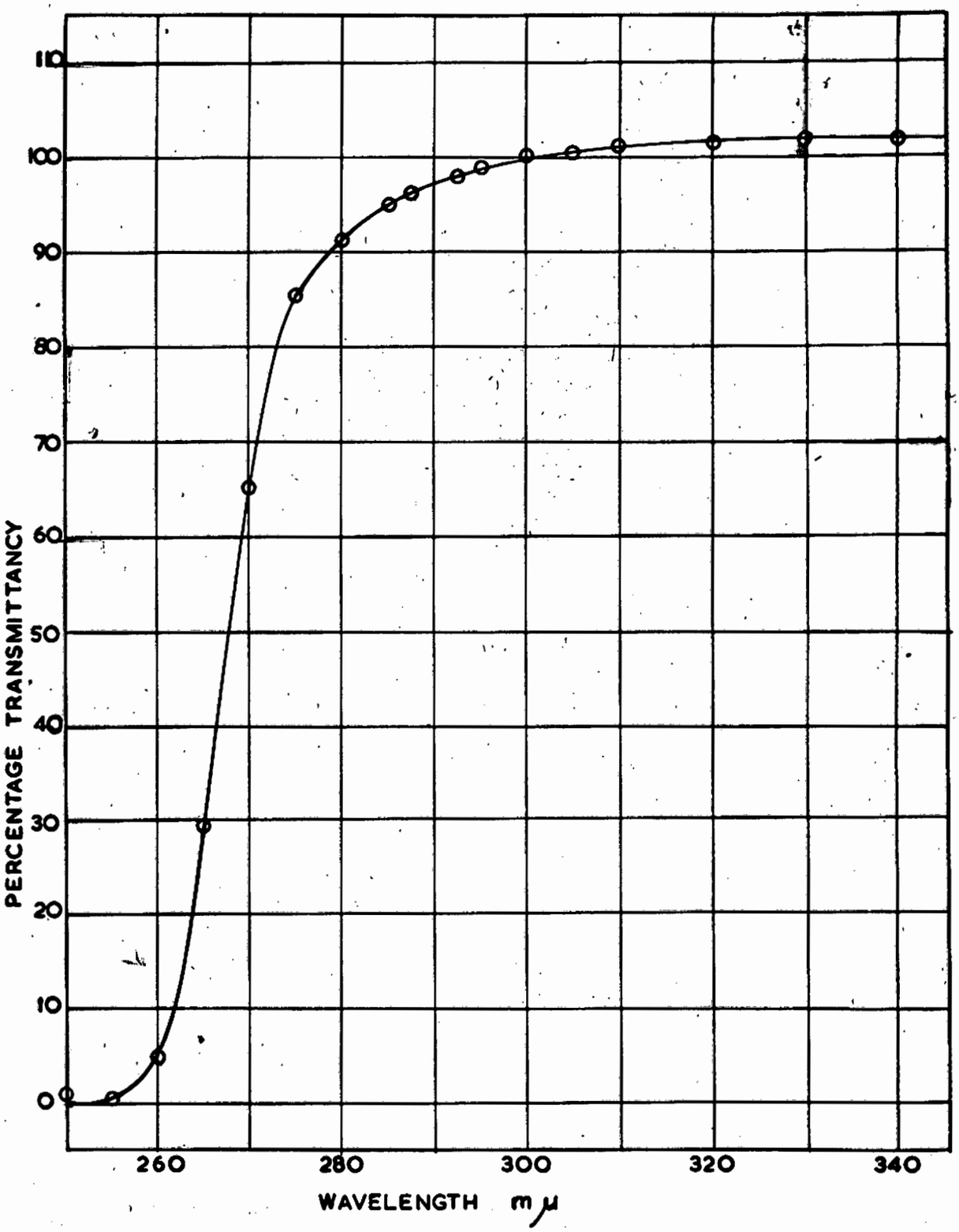
PERCENTAGE TRANSMITTANCY
110
100
90
80
70
60
50
40
30
20
10
0
260
280
300
320
340
WAVELENGTH mμ

FIGURE XIV

was standardised against the dioxan by titrating a fixed volume (2 ml.) of the latter, and then titrating 2 ml. portions of several solutions of water in dioxan of accurately known concentration. The actual volume of Karl Fischer reagent required for the added water in each case was calculated by subtracting the number of ml. of it used by the 2 ml. dioxan from the total number of ml. used for the solution of water in dioxan. A graph (Figure XV) was drawn of ml. Karl Fischer Reagent against weight of water. This proved to be the expected straight line, from which the weight of water present in a larger volume of dioxan (10 ml.) was read off. The results obtained are shown in Table II.

TABLE II.

Volume of Karl Fischer Reagent equivalent to known concentrations of water.

Concentration of water in dioxan in g. per 2 ml.	ml. Karl Fischer Reagent for 2 ml. dioxan	ml. Karl Fischer Reagent for 2 ml. water in dioxan	∴ ml. Karl Fischer Reagent for added water
.001420	2.45	3.00	0.55
.007478	2.45	4.47	2.02
.014956	2.45	6.34	3.89
.022435	2.45	8.26	5.81
.026920	2.45	9.26	6.81
.029913	2.45	10.30	7.85
.044870	2.45	14.16	11.65

10 ml. dioxan ≡ 12.02 ml. Karl Fischer Reagent

∴ From graph (Figure XV)

10 ml. dioxan ≡ .045 g. water

∴ %age water in dioxan = 0.45%.

(c) Attempted preparations of the methochloride of benzaldazine.

Methylhydrazine hydrogen sulphate, CH_3NHNH_2, H_2SO_4, was available as starting material. This was converted to the chloride by adding the stoichiometric quantity of barium chloride to precipitate all the sulphate, filtering and evaporating the filtrate

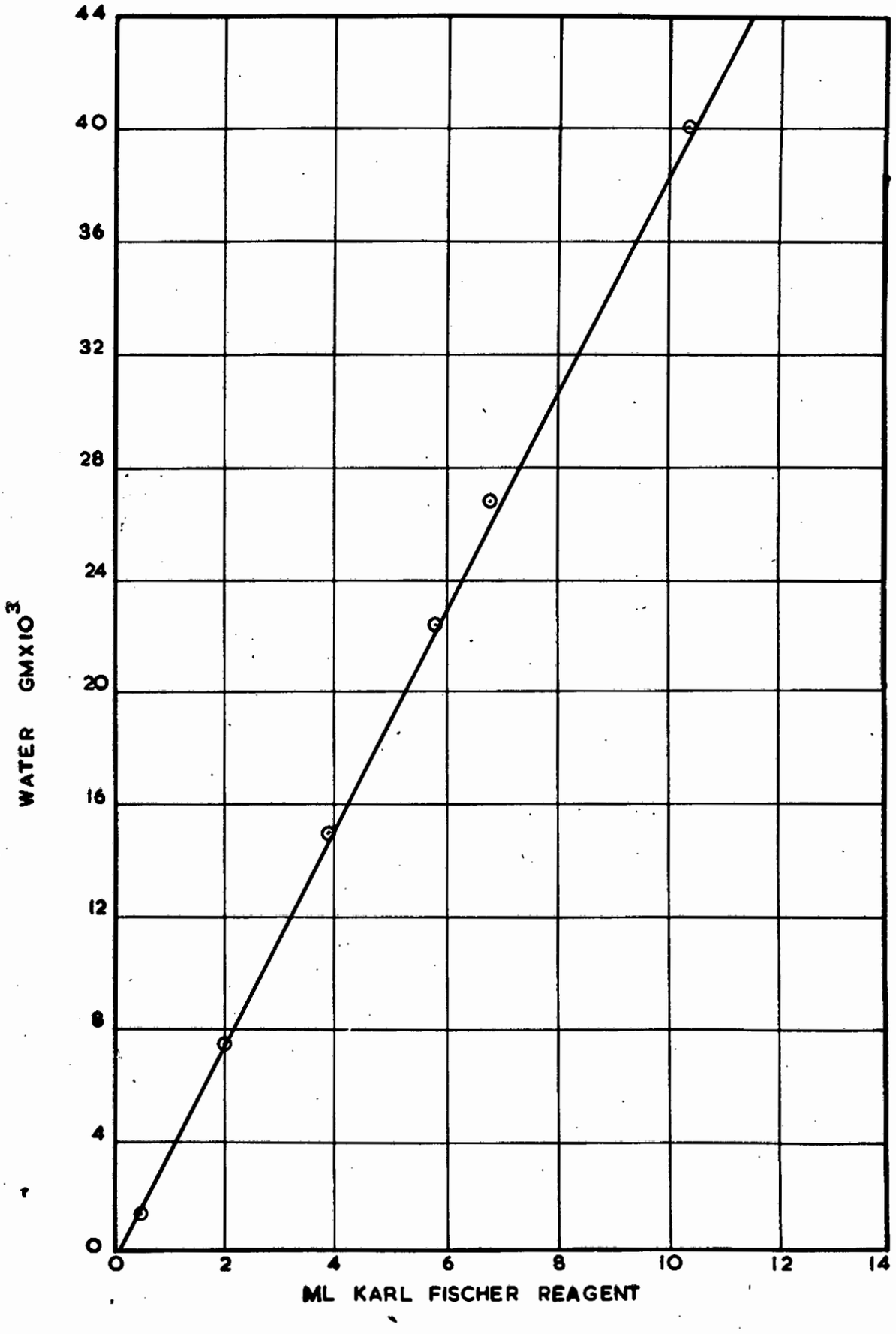
WATER GMX10³
0
4
8
12
16
20
24
28
32
36
40
44
0
2
4
6
8
10
12
14
ML KARL FISCHER REAGENT

FIGURE XV

to near dryness, and adding ethanol. After filtering again the methylhydrazine dihydrochloride content of the solution was determined on an aliquot by an iodate titration, and the stoichiometric quantity of benzaldehyde then added to precipitate the metho-salt of the azine. No precipitate formed either on evaporation or on adding ether.

The second attempt was to grind a sample of methylhydrazine hydrogen sulphate to a paste with the stoichiometric quantity of barium carbonate, to extract the paste with ether and to dry the extract with potassium carbonate. After filtering an excess of dry hydrogen chloride was passed through the ethereal solution. Precipitation of methylhydrazinedihydrochloride occurred, its purity being checked by hydrazine and chloride determinations. Many unsuccessful attempts, using various solvents, were made to condense benzaldehyde on to the methochloride, but in all cases no crystalline product was obtained.

The optical density of a saturated solution of methylhydrazine-dihydrochloride in dioxan containing a small concentration of benzaldehyde was determined. (See Table III).

TABLE III.

Optical density of a solution of methylhydrazine hydrochloride and benzaldehyde in dioxan.

Wave length in mμ	Extinction
270	.462
275	.515
277	.538
280	.581
281	.588
282	.588
283	.584
284	.570
285	.560
286	.556
288	.552
289	.550
290	.540
292	.502
295	.411

(d) The optical densities of benzaldehyde and of its hydrazone in dioxan solution.

The optical densities of solutions in dioxan of benzaldehyde and of its hydrazone (prepared by the method of Curtius and Phlug[13]) were determined. The results obtained are shown in Table IV.

TABLE IV.

Optical density of benzaldehyde and of benzalhydrazone in dioxan solution.

Wave length in mμ	Molecular Extinction coefficient x 10^{-4} of benzaldehyde	Molecular Extinction coefficient x 10^{-4} of benzalhydrazone
270	0.831	1.393
275	0.931	1.730
277	0.957	1.820
280	0.995	1.951
282	1.000	1.991
284	0.914	1.950
286	0.871	1.820
288	0.801	1.656
290	0.773	1.420
292	0.631	1.047
294	0.428	0.661
298	0.251	0.457
300	0.135	0.296
302	0.062	0.171

(e) The optical densities of benzaldazine and of its hydrochloride in dioxan solution.

The optical densities of benzaldazine and of its hydrochloride in dioxan solution were determined at 25.5 ± 0.5°C in a Beckmann D.U. Spectrophotometer. The maximum possible accuracy was used in preparing the solutions, a micro-balance and Grade A pipettes and standard flasks being utilized. Readings of optical density were commenced at a wave length of 270 mμ within five minutes of preparing the solutions. Great care was exercised in cleaning the cells, the optically smooth surfaces being carefully polished before use and care taken not to handle them thereafter. The temperature was controlled by means of two metal compartments fixed on each side of the cell compartment. These had been constructed by W.G. Davies[21], and were designed by him to allow water from a thermostat to circulate through them. In the centre of each compartment was a circular aperture

through which the light could pass. The compartments were held in place by long screws in a similar fashion to which the cell compartment is usually held. This arrangement was found to control the temperature inside the cells to within 0.5°C.

Tables IV and V below show the optical densities of benzaldazine and of its hydrochloride. Three readings of optical density at each wave length are shown, these being taken with samples from different preparations. In the last columns of the tables the mean value of the optical density at a fixed wave length is shown together with its standard deviation.

TABLE V.

Optical density of benzaldazine in dioxan solution at 25.5 ± 0.5°C.

Wave length in mμ	Molecular extinction coefficient of benzaldazine, $K_B \times 10^{-5}$	Mean value of K x 10^{-5} and its standard deviation x 10^{-5}
270	0.134; 0.150; 0.155	0.146 ± 0.011
275	0.177; 0.184; 0.189	0.183 ± 0.006
280	0.214; 0.220; 0.223	0.219 ± 0.005
282	0.229; 0.233; 0.242	0.235 ± 0.007
284	0.243; 0.246; 0.255	0.248 ± 0.006
286	0.262; 0.264; 0.272	0.266 ± 0.005
288	0.280; 0.283; 0.292	0.285 ± 0.006
290	0.300; 0.307; 0.313	0.307 ± 0.007
292	0.313; 0.316; 0.321	0.317 ± 0.004
294	0.321; 0.326; 0.332	0.326 ± 0.005
296	0.326; 0.336; 0.341	0.334 ± 0.008
297	0.336; 0.339; 0.347	0.341 ± 0.006
298	0.338; 0.346; 0.348	0.344 ± 0.005
299	0.343; 0.353; 0.355	0.350 ± 0.006
300	0.351; 0.358; 0.361	0.357 ± 0.005
301	0.354; 0.365; 0.366	0.362 ± 0.006
302	0.356; 0.368; 0.369	0.364 ± 0.007
303	0.354; 0.366; 0.366	0.362 ± 0.007
304	0.349; 0.360; 0.362	0.357 ± 0.007
305	0.343; 0.352; 0.352	0.349 ± 0.005
306	0.335; 0.347; 0.339	0.340 ± 0.006
307	0.324; 0.336; 0.326	0.329 ± 0.006
308	0.321; 0.335; 0.325	0.327 ± 0.007
309	0.316; 0.329; 0.321	0.322 ± 0.006
310	0.310; 0.323; 0.318	0.317 ± 0.006
311	0.314; 0.322; 0.320	0.319 ± 0.004
312	0.314; 0.322; 0.320	0.319 ± 0.004
313	0.314; 0.322; 0.320	0.319 ± 0.004
314	0.308; 0.318; 0.313	0.313 ± 0.005
315	0.304; 0.314; 0.310	0.309 ± 0.005
316	0.296; 0.306; 0.302	0.300 ± 0.005
318	0.255; 0.269; 0.265	0.263 ± 0.007
320	0.220; 0.234; 0.227	0.228 ± 0.007

TABLE VI.

Optical density of benzaldazine hydrochloride in dioxan solution at 25.5 ± 0.5°C.

Wave length in mμ	Molecular extinction coefficient of benzaldazine hydrochloride, K x 10^{-5}	Mean value of K x 10^{-5} and its standard deviation x 10^{-5}
270	0.160; 0.145; 0.163	0.156 ± 0.012
275	0.185; 0.194; 0.199	0.193 ± 0.007
280	0.223; 0.231; 0.236	0.230 ± 0.006
282	0.236; 0.245; 0.247	0.243 ± 0.005
284	0.254; 0.258; 0.265	0.259 ± 0.006
286	0.270; 0.278; 0.283	0.277 ± 0.007
288	0.287; 0.294; 0.296	0.292 ± 0.005
290	0.300; 0.310; 0.314	0.308 ± 0.007
291	0.305; 0.314; 0.317	0.312 ± 0.006
292	0.310; 0.319; 0.319	0.316 ± 0.005
294	0.318; 0.324; 0.333	0.325 ± 0.008
296	0.331; 0.328; 0.337	0.332 ± 0.005
298	0.343; 0.342; 0.353	0.346 ± 0.006
299	0.350; 0.346; 0.354	0.350 ± 0.004
300	0.355; 0.352; 0.364	0.357 ± 0.006
301	0.362; 0.354; 0.357	0.358 ± 0.004
302	0.363; 0.357; 0.369	0.363 ± 0.006
303	0.358; 0.355; 0.365	0.359 ± 0.005
304	0.345; 0.345; 0.360	0.350 ± 0.008
305	0.341; 0.342; 0.352	0.345 ± 0.006
307	0.322; 0.332; 0.336	0.330 ± 0.005
308	0.318; 0.326; 0.331	0.325 ± 0.007
309	0.312; 0.320; 0.326	0.319 ± 0.007
310	0.312; 0.311; 0.322	0.315 ± 0.006
311	0.312; 0.323; 0.329	0.321 ± 0.008
312	0.313; 0.318; 0.325	0.319 ± 0.007
313	0.315; 0.318; 0.323	0.319 ± 0.004
314	0.308; 0.314; 0.314	0.312 ± 0.004
315	0.303; 0.305; 0.310	0.306 ± 0.004
318	0.266; 0.258; 0.265	0.263 ± 0.004
320	0.224; 0.227; 0.235	0.229 ± 0.006
325	0.162; 0.163; 0.176	0.167 ± 0.008

(f) The optical densities of benzaldazine in dioxan solution containing varying concentrations of hydrogen chloride, and of the benzaldazinium ion.

The changes in optical density with time of solutions of fixed benzaldazine concentration and varying hydrogen chloride concentrations were determined in the first place at the wave lengths 275, 280, 283, 285, 288, 290, 295, 300, 310 and 315 mμ. Measurements were made in solutions in dioxan containing hydrogen chloride of molarities 0.341, 0.682 and 1.262. The results obtained are shown in Table VII.

TABLE VII.

Change in optical density with time of a solution of .0000373 M benzaldazine in dioxan containing hydrogen chloride.

Molarity HCl 0.341										
Wave length in mμ	275	280	283	285	288	290	295	300	310	315
time min.	2	3	4	5	6	7	8	9	10	11
log ε	4.053	4.126	4.158	4.171	4.177	4.169	4.127	4.059	3.830	3.627
time min.	12	13	14	15	16	17	18	19	20	21
log ε	4.108	4.145	4.150	4.143	4.134	4.109	3.825	3.664	3.442	3.310
time min.	22	23	24	25	26	27	28	29	30	31
log ε	4.045	4.083	4.086	4.055	4.014	3.943	3.530	3.375	3.173	3.066
time min.	32	33	34	35	36	37	38	39	40	41
log ε	3.805	3.870	3.869	3.840	3.801	3.722	3.236	3.090	-	-
time min.	42	43	44	45	46	47	48	49	50	51
log ε	3.580	3.621	3.652	3.609	3.603	3.512	-	-	-	-
time min.	52	53	54	55						
log ε	3.432	3.470	3.521	3.541	-	-	-	-	-	-

Molarity HCl 0.682										
time min.	2	3	4	5	6	7	8	9	10	11
log ε	3.932	4.008	4.036	4.062	4.090	4.090	4.053	3.991	3.809	3.624
time min.	12	13	14	15	16	17	18	19	20	21
log ε	3.987	4.041	4.050	4.048	4.039	4.012	3.586	3.486	3.381	3.211
time min.	22	23	24	25	26	27	28	29	30	31
log ε	3.911	3.964	3.965	3.964	3.945	3.915	3.204	3.193	-	-
time min.	32	33	34	35	36	37	38	39	40	41
log ε	3.620	3.672	3.710	3.706	3.699	3.650	-	-	-	-
time min.	42	43	44	45	46	47	48	49	50	51
log ε	3.331	3.380	3.402	3.417	3.421	3.359	-	-	-	-
time min.	52	53	54	55	56					
log ε	3.214	3.258	3.304	3.343	3.324	-	-	-	-	-

Molarity HCl 1.262										
time min.	2	3	4	5	6	7	8	9	10	11
log ε	3.842	3.956	4.016	4.054	4.066	4.081	4.072	4.033	3.936	3.832
time min.	12	13	14	15	16	17	18	19	20	21
log ε	3.975	4.040	4.059	4.063	4.061	4.031	3.991	3.903	3.710	3.402
time min.	22	23	24	25	26	27	28	29	30	31
log ε	3.938	3.978	4.001	4.005	3.998	3.962	3.902	3.782	3.423	-
time min.	32	33	34	35	36	37	38	39	40	41
log ε	3.540	3.732	3.743	3.730	3.715	3.698	3.611	3.509	3.211	-

In order to follow more accurately the change in log ε with time, it was decided to cut down the number of wave lengths for measurements from ten to five, thus obtaining readings of log ε at each wave length at five minutely intervals. Measurements were carried out over as wide a range of concentrations of hydrogen chloride as possible. The results obtained are shown in Table VIII.

TABLE VIII.

Change in optical density with time at wave lengths 280, 285, 290, 295 and 300 mμ of a solution of .0000373 M benzaldazine in dioxan containing hydrogen chloride.

(i) Molarity HCl = 0.036										
time min.	2	7	12	17	22	27	32	37	42	47
log ε_{280}	4.279	4.277	4.233	4.175	4.128	4.071	4.015	3.966	3.914	3.871
time min.	3	8	13	18	23	28	33	38	43	48
log ε_{285}	4.318	4.274	4.215	4.154	4.102	4.043	3.986	3.931	3.882	3.833
time min.	4	9	14	19	24	29	34	39	44	49
log ε_{290}	4.322	4.248	4.176	4.110	4.056	3.994	3.928	3.876	3.823	3.775
time min.	5	10	15	20	25	30	35	40	45	50
log ε_{295}	4.286	4.185	4.098	4.025	3.963	3.892	3.830	3.765	3.710	3.646
time min.	6	11	16	21	26	31	36	41	46	51
log ε_{300}	4.229	4.095	3.988	3.919	3.849	3.771	3.707	3.622	3.565	3.482
(ii) Molarity HCl = 0.066										
time min.	2	7	12	17	22	27	32	37	42	47
log ε_{280}	4.291	4.280	4.231	4.175	4.111	4.050	3.986	3.935	4.882	3.835
time min.	3	8	13	18	23	28	33	38	43	48
log ε_{285}	4.314	4.272	4.229	4.159	4.090	4.023	3.965	3.909	3.850	3.803
time min.	4	9	14	19	24	29	34	39	44	49
log ε_{290}	4.314	4.241	4.180	4.117	4.050	3.978	3.917	3.858	3.800	3.753
time min.	5	10	15	20	25	30	35	40	45	50
log ε_{295}	4.264	4.178	4.102	4.038	3.957	3.885	3.814	3.747	3.677	3.622
time min.	6	11	16	21	26	31	36	41	46	51
log ε_{300}	4.191	4.090	4.003	3.931	3.849	3.773	3.696	3.619	3.546	3.485
(iii) Molarity of HCl = 0.113										
time min.	2, 3	7	12	17	22	27	32	37	42	
log ε_{280}	4.205, 4.215	4.199	4.126	4.052	3.968	3.894	3.825	3.761	3.705	
time min.	3	8	13	18	23	28	33	38	43	
log ε_{285}	4.238	4.193	4.113	4.026	3.940	3.869	3.798	3.727	3.669	
time min.	4	9	14	19	24	29	34	39	44	
log ε_{290}	4.229	4.159	4.072	3.976	3.897	3.821	3.747	3.674	3.605	

time min.	5	10	15	20	25	30	35	40	45
log ε_{295}	4.165	4.071	3.987	3.882	3.788	3.693	3.613	3.518	3.437
time min.	6	11	16	21	26	31	36	41	46
log ε_{300}	4.071	3.975	3.871	3.759	3.654	3.549	3.450	3.342	3.228

(iv) Molarity of HCl = 0.209

time min.	2.	7	12	17	22	27	32	37	42
log$\varepsilon\varepsilon_{280}$	4.192	4.193	4.099	3.994	3.904	3.812	3.734	3.664	3.610
time min.	3	8	13	18	23	28	33	38	43
log ε_{285}	4.241	4.184	4.083	3.975	3.879	3.783	3.700	3.633	3.568
time min.	4	9	14	19	24	29	34	39	44
log ε_{290}	4.235	4.145	4.039	3.935	3.823	3.729	3.638	3.559	3.500
time min.	5	10	15	20	25	30	35	40	45
log ε_{295}	4.186	4.069	3.944	3.932	3.689	3.581	3.450	3.358	3.255
time min.	6	11	16	21	26	31	36	41	46
log ε_{300}	4.110	4.959	3.826	3.689	3.536	3.406	3.255	3.101	2.960

(v) Molarity HCl = 0.48

time min.	2, 3½	7	12	17	22	27	32	37
log ε_{280}	4.124, 4.155	4.123	3.975	3.828	3.703	3.610	3.552	3.532
time min.	3	8	13	18	23	28	33	38
log ε_{285}	4.176	4.089	3.946	3.785	3.651	3.565	3.508	3.482
time min.	4	9	14	19	24	29	34	39
log ε_{290}	4.184	4.059	3.895	3.721	3.587	3.489	3.429	3.406
time min.	5	10	15	20	25	30	35	40
log ε_{295}	4.152	3.968	3.786	3.572	3.392	3.228	3.177	3.161
time min.	6	11	16	21	26	31	36	41
log ε_{300}	4.083	4.845	4.646	3.388	3.189	2.973	2.844	

(vi) Molarity HCl = 0.54

time min.	2	7	12	17	22	27	32
log ε_{280}	4.109	4.075	3.910	3.771	3.641	3.559	3.518
time min.	3	8	13	18	23	28	33
log ε_{285}	4.170	4.064	3.863	3.723	3.602	3.515	3.446
time min.	4	9	14	19	24	29	34
log ε_{290}	4.181	4.006	3.812	3.651	3.515	3.429	3.383
time min.	5	10	15	20	25	30	35
log ε_{295}	4.134	3.906	3.686	3.446	3.363	3.199	3.062
time min.	6	11	16	21	26	31	36
log ε_{300}	4.018	3.785	3.529	3.261	3.082	2.844	2.751

From the results in Tables VII and VIII the graphs of log ε against time for each wave length, for the same azine and for various acid concentrations were plotted. One such set of curves (for molarity of hydrogen chloride = 0.036) is shown in Figure I, page 14a .

From these plots the values of log ε at zero time (log ε_0) at a fixed wave length of 280 mμ, was estimated by extrapolation (see Figure I, page 14a, and Figure VIII, page 25a) for the various concentrations of hydrogen chloride. The "trend" graphs were drawn of the values of log ε_0 thus obtained against (i) the molarity of the hydrogen chloride in the dioxan solution and (ii) the corresponding acidity function of the hydrogen chloride in dioxan, read off from the curve shown in Figure VI, page 23a. These values of log $\varepsilon_{0_{280}}$ are shown in Table IX, and the "trend" curves in Figure II, page 15a.

Further, from the above mentioned plots of log ε against time for the wave length 280 mμ, the maximum value of log ε (log ε_{max}) attained at any time was read off. These values of log ε_{max} for each concentration of hydrogen chloride are also shown in Table IX, together with the difference between log ε_{max} and the corresponding value of log ε_0. These differences, Δ log ε, are shown in the last column of Table IX, and are shown plotted (i) against the corresponding molarity of the hydrogen chloride in the dioxan and (ii) against the corresponding acidity function in Figure IV, page 18a.

TABLE IX.

The logarithms of the extinctions at zero time, log ε_0, the maximum value of the logarithms of the extinctions, log ε_{max}, and the differences between them, Δ log ε, at a fixed wave length of 280 mμ for solutions of fixed benzaldazine but varying hydrogen chloride concentrations.

Molarity of hydrogen chloride in dioxan	Acidity Function of hydrogen chloride in dioxan	log ε_0	log ε_{max}	Δ log ε
.036	1.60	4.266	4.29	.02
.066	1.44	4.275	4.29	.01
.113	1.33	4.150	4.21	.06
.209	1.14	4.140	4.22	.08
.341	1.04	4.095	4.17	.07
.480	1.00	4.050	4.16	.11
.540	0.97	4.030	4.13	.10
.682	0.90	3.960	4.06	.095
1.262	0.40	3.900	4.05	.15

From the plots of the results shown in Tables VII and VIII (an example of which is shown in Figure I for a 0.036 molar hydrogen chloride solution) curves were drawn of log ε against wave length at fixed times. An example of the curves thus obtained is shown in Figure III, page 16a, for a 0.341 molar hydrogen chloride solution, where the time intervals 5, 9, 12, 22, 27 and 32 minutes were chosen. The values of log ε at the various times for molarities of hydrogen chloride in dioxan of 0.341, 0.682 and 1.262 in solutions of the same concentration of azine are shown in Tables X(i), X(ii) and X(iii) respectively. The corresponding values of log ε at fixed times for the solutions at the other molarities of hydrogen chloride (see Table VIII (i) to (vi)) are not shown, as for these solutions the changes in log ε with time at only five different wave lengths had been noted. This meant that the resulting absorption curves would be restricted to a more limited wave length range.

TABLE X.

Values of log ε at fixed times over the wave length range 275 to 315 mμ for a .0000373 M solution of benzaldazine in dioxan containing hydrogen chloride.

(i) Molarity of hydrogen chloride = 0.341

Time in min.	Wave length in mμ									
	275	280	283	285	288	290	295	300	310	315
5	4.078	4.134	4.165	4.173	4.180	4.166	4.210	4.300	4.200	3.900
9	4.103	4.152	4.170	4.165	4.170	4.156	4.095	4.058	3.990	3.790
12	4.108	4.149	4.160	4.157	4.160	4.140	4.000	3.860	3.680	3.580
22	4.045	4.090	4.104	4.083	4.073	4.033	3.702	3.580	3.385	3.280
27	4.036	4.020	4.041	4.015	4.000	3.940	3.550	3.430	3.250	3.150
32	3.805	3.890	3.920	3.900	3.880	3.830	3.442	3.290	3.120	3.015

(ii) Molarity of hydrogen chloride = 0.682

5	3.967	4.020	4.042	4.062	4.094	4.098	4.185	-	4.030	3.895
9	3.988	4.039	4.054	4.070	4.080	4.075	3.995	3.991	3.850	3.710
12	3.988	4.042	4.052	4.065	4.060	4.055	3.860	3.810	3.720	3.600
22	3.911	3.980	3.995	4.000	3.992	3.970	3.400	3.370	3.280	3.184
27	3.770	3.870	3.915	3.912	3.930	3.915	3.235	3.220	3.050	-
32	3.620	3.700	3.775	3.774	3.800	3.800	3.145	3.145	-	-

(iii) Molarity of hydrogen chloride = 1.262

5	3.890	3.950	4.025	4.055	4.060	4.072	4.090	4.075	4.090	-
9	3.949	4.200	4.048	4.070	4.075	4.084	4.073	4.033	3.960	3.930
12	3.975	4.038	4.060	4.070	4.078	4.080	4.000	3.997	3.875	3.780
22	3.938	3.990	4.021	4.035	4.033	4.010	3.960	3.870	3.650	3.388
27	3.810	3.895	3.940	3.972	3.982	3.962	3.910	3.810	3.512	-
32	3.540	3.780	3.785	3.845	3.872	3.835	3.830	3.705	3.380	-

The values of the specific extinctions after twelve minutes of solutions of fixed benzaldazine concentration were obtained from the plots of log ε against time for molarities of hydrogen chloride of 0.341, 0.682 and 1.262. These figures are shown in Table XI.

TABLE XI.

Optical Densities of Benzaldazine Hydrochloride in dioxan solution containing dry hydrogen chloride.

Wave length in mμ	Specific extinction x 10^{-5} after 12 mins. in 0.341 M HCl	Specific extinction x 10^{-5} after 12 mins. (0.682 M HCl)	Specific extinction x 10^{-5} after 12 mins. 1.262 M HCl
275	0.128	0.097	0.094
280	0.141	0.110	0.109
283	0.145	0.113	0.115
285	0.147	0.117	0.118
288	0.144	0.115	0.119
290	0.138	0.111	0.120
295	0.127	0.102	0.110
300	0.105	0.089	0.100
310	0.064	0.056	0.076
315	0.041	0.038	0.060

Plots were made of the figures in Table XI, and the three curves thus obtained were taken as representing the true shape of the benzaldazinium ion absorption curve. The justification for this has been discussed on pages 14-20. The three curves thus obtained were drawn to pass through the point of cut of the absorption curves of benzaldazine and of its hydrochloride, giving curves IV, V, and VI in Figure V, page 19a. The resulting values for the molecular extinction coefficients for the benzaldazinium ion are shown in Table XII.

In Table XIII, below, the values for the molecular extinctions of benzaldazine, benzaldazine hydrochloride and for the benzaldazinium ion, together with their respective standard deviations are given over the wave length range of 275 to 288 mμ, for a solution of fixed benzaldazine concentration. In the last column of Table XIII the calculated value for K_b for each wave length is shown, together with its calculated standard deviation. The mean value of K_b over the whole wave length range was found to be 0.11 with an apparent standard

deviation of ± .035. The calculated deviations, however, show that the results obtained at the lower wave lengths (<284 m) are the more reliable, since they have lower standard deviations. The mean obtained for K_b over the lower wave length range 275 to 284 was 0.10 ± .08, (calculated standard deviation). However, as the difference between this value and the value 0.11 obtained when using the results for the wave length range 275 to 288 mμ, is so small compared to the standard deviations, it is immaterial which value of K_b is chosen. At best this method can only give the relative order of magnitude of K_b.

TABLE XII.
Optical density of benzaldazinium ion.

Wave length mμ	Molecular extinction coefficient $K_{BH^+} \times 10^{-5}$			Mean $K_{BH^+} \times 10^{-5}$ and its standard deviation x 10^{-5}
	From Curve IV	From Curve V	From Curve VI	
275	0.324	0.321	0.309	0.318 ± 0.078
276	0.326	0.324	0.313	0.321 ± 0.072
277	0.329	0.326	0.316	0.324 ± 0.068
278	0.332	0.329	0.319	0.327 ± 0.068
279	0.335	0.332	0.322	0.330 ± 0.068
280	0.337	0.334	0.324	0.332 ± 0.068
281	0.339	0.335	0.326	0.333 ± 0.067
282	0.340	0.336	0.328	0.334 ± 0.062
283	0.341	0.336	0.329	0.335 ± 0.060
284	0.344	0.338	0.331	0.337 ± 0.066
285	0.350	0.339	0.332	0.400 ± 0.067
286	0.344	0.340	0.333	0.339 ± 0.056
287	0.343	0.340	0.334	0.339 ± 0.041
288	0.341	0.338	0.334	0.334 ± 0.057

TABLE XIII.

Calculated value of $K_b = \dfrac{K - K_B}{K_{BH^+} - K}$

Wave length mμ	K x 10^{-5} and its standard deviation	K_B x 10^{-5} and its standard deviation	K_{BH^+} x 10^{-5} and its standard deviation	K_b and its calculated standard deviation
275	0.193 ± 0.007	0.183 ± 0.006	0.318 ± 0.078	0.080 ± 0.077
276	0.199	0.189	0.321 ± 0.072	0.082
277	0.207	0.196	0.324 ± 0.068	0.094
278	0.214	0.204	0.327 ± 0.068	0.088
279	0.222	0.212	0.330 ± 0.068	0.091
280	0.229 ± 0.006	0.219 ± 0.005	0.332 ± 0.068	0.097 ± 0.080
281	0.237	0.227	0.333 ± 0.067	0.104
282	0.242 ± 0.005	0.235 ± 0.007	0.334 ± 0.062	0.076 ± 0.108
283	0.250	0.242	0.335 ± 0.060	0.094
284	0.259 ± 0.006	0.248 ± 0.006	0.337 ± 0.066	0.140 ± 0.116
285	0.268	0.251	0.400 ± 0.067	0.129
286	0.277 ± 0.007	0.266 ± 0.005	0.339 ± 0.056	0.177 ± 0.175
287	0.284	0.275	0.339 ± 0.041	0.164
288	0.292 ± 0.005	0.285 ± 0.006	0.334 ± 0.057	0.166 ± 0.226
			Mean =	0.11 ± 0.035

3. Experimental evidence on which the mechanism of the hydrolysis of benzaldazine in the presence of acid was based.

(a) Results showing the effect of added water on the rate of the reaction occurring between benzaldazine and hydrogen chloride in dioxan solution.

In Table XIV(i) and (ii) are shown the values, at regular time intervals, of the logarithms of the extinctions at 295 mμ [Table XIV(i)] and at 300 mμ [Table XIV(ii)] of solutions in dioxan of fixed benzaldazine and of fixed hydrogen chloride concentrations, to which varying quantities of water have been added. The plots of the figures in Table XIV(ii) are shown in Figure VII, page 24a.

TABLE XIV

Logarithm of extinction of .000049 M benzaldazine and 0.10 M hydrogen chloride in dioxan to which known quantities of water have been added.

(i) λ = 295 mμ

Molarity of added water	.000098	.000196	.000294	.000392	.000686
Time in min.	log ε x10^{-4}	log ε x10^{-4}	log ε x10^{-4}	log ε x10^{-4}	log ε x10^{-4}
2	.950	.969	.963	.958	.963
4	.880	.892	.897	.881	.887
6	.825	.835	.833	.818	.814
8	.777	.775	.772	.757	.747
10	.726	.715	.710	.699	.690
12	.676	.654	.658	.646	.631
14	.633	.610	.599	.593	.571
16	.583	.553	.549	.538	.519
18	.539	.504	.500	.481	.468
20	.500	.459	.450	.436	.420
22	.455	.407	.403	.384	.377
24	.420	.358	.354	.337	.328
26	.375	-	.316	.288	.288
28	.337	-	-	.241	.225
30	.303	-	-	.196	.201

(ii) λ = 300 mμ

Molarity of added water	.000098	.000196	.000294	.000392	.00686
Time in min.	log ε x10^{-4}	log ε x10^{-4}	log ε x10^{-4}	log ε x10^{-4}	log ε x10^{-4}
2	.883	.903	.903	.883	.887
4	.800	.806	.799	.785	.780
6	.725	.725	.723	.708	.700
8	.667	.656	.655	.643	.633
10	.612	.593	.589	.579	.560
12	.559	.542	.532	.521	.505
14	.509	.473	.474	.462	.446
16	.458	.423	.413	.400	.391
18	.408	.367	.364	.342	.322
20	.362	.310	.310	.283	.279
22	.314	.263	.243	.228	.230
24	.265	.215	.193	.173	.164
26	.223	.176	.155	.111	.117
28	.182	-	-	.061	.068
30	.143	-	-	-	.025

(b) The determinations of the first order velocity constants for the hydrolysis of benzaldazine hydrochloride to benzalhydrazone and benzaldehyde in dioxan solution containing hydrogen chloride.

Plots were made of the values of log ε at 295 mμ, at various time intervals, of solutions in dioxan of the same azine but varying hydrogen chloride concentrations. The values of log ε were obtained from the results shown in Tables VII and VIII, and the graphs drawn are shown in Figure IX. From these graphs the first order velocity constants were obtained for each concentration of hydrogen chloride, by measuring the slopes of the linear portions of the curves. Table XV shows the relationship between the first order velocity constants thus obtained, and the acidity functions of the corresponding solutions of hydrogen chloride in dioxan.

TABLE XV.

Molarity of hydrogen chloride in dioxan	Acidity Function, Ho, of hydrogen chloride in dioxan	First order velocity const., K, in min^{-1}	log K	log K + Ho
.036	1.62	0.0061	-2.22	-.60
.066	1.44	0.0063	-2.20	-.76
.113	1.33	0.0079	-2.10	-.77
.209	1.14	0.0122	-1.91	-.77
.341	1.04	0.0128	-1.89	-.85
.480	1.00	0.0165	-1.78	-.78
.540	0.97	0.0185	-1.73	-.76
.682	0.90	0.0206	-1.69	-.79

IV. CONCLUSION.

The salt forming properties of the aldazines have been surveyed, and a complete series of the complex salts of the aromatic aldazines benzaldazine, anisaldazine and salicylaldazine has been prepared[22]. These salts show the expected gradation in colour and melting point. The chloro-salts are lightly coloured, the bromo-salts yellow or orange, and the iodo-salts red; the melting point rises with increasing complexity of the base for any one anion, with increasing atomic weight of the halogen for the same base and metal, and with increasing atomic weight of the metal for the same base and halogen. The chloro-complexes are readily hydrolysed in water, smelling of aldehyde in moist air, but the bromo- and the iodo-complexes, especially, are decomposed with difficulty by boiling hydrochloric acid. The salts are insoluble in cyclohexane, ether and xylene, and sparingly soluble in nitrobenzene, dioxan and pyridine. Some simple salts (hydrohalides and sulphates) of the same aldazines were prepared and were also found to be readily hydrolysed in the presence of water. Crystalline salts were not obtained from aliphatic aldazines, which tended to polymerise before forming salts.

One crystalline compound, of empirical formula $C_{22}H_{40(42)}N_4O_6SnCl_6$, was prepared from acetaldehyde and hydrazine chlorostannate. Its structural formula was not obtained but some preliminary results for this purpose were recorded. The full elucidation of its complex structure should provide an interesting field for further investigation.

"Mixed" azines, containing one mol. of each of aromatic aldehyde and of acetone condensed per mol. of hydrazine, readily formed simple salts.

One co-ordination compound formed from stannic chloride (1 mol.) and salicylaldazine (2 mols.) was prepared, and it was noted that stannic, antimony and bismuth chlorides tended to form such compounds with the aromatic azines. A systematic study of these compounds and

in particular of their structures should also prove an interesting field for further investigation.

The presence of the benzaldazinium ion in dioxan solution containing hydrogen chloride has been established, and as this is the first evidence for the existence of an aldazinium or a ketazinium ion in solution, it has been taken as justification for describing the series of compounds prepared above as "salts".

The ionization constant as a base of benzaldazine has not been determined exactly, but the relative order of its magnitude has been established. The doubt as to the reliability of the absolute values of the acidity functions of solutions of hydrogen chloride in dioxan, as reported by Braude[19], has meant that the spectrophotometric method could not be expected to yield an absolute value for the ionization constant of benzaldazine. It was considered inadvisable to attempt to extend James and Knox[18] measurements of Ho for hydrogen chloride in dioxan, in order to determine their absolute values, as even if the latter were established, only a range of values for the ionization constant of benzaldazine would be obtainable by the spectrophotometric method. This was due to the small differences between the absorption curves for the azine and for its hydrochloride.

A mechanism for the hydrolysis of benzaldazine hydrochloride to benzaldehyde and hydrazine hydrochloride has been suggested, but no confirmation of its validity has been obtained. However a preliminary kinetic investigation of the hydrolysis showed it to be of the first order with respect to the benzaldazine concentration, and also showed that its first order velocity constant, K, was directly proportional to proton availability. This proportionality of K with Braude's values for proton availability (i.e. for his values of the acidity functions of dioxan containing varying concentrations of hydrogen chloride) confirm the relative magnitudes of Braude's values. At the worst a constant correction may have to be made to all his values of Ho. Further kinetic investigations were

not carried out as it was obvious that although the concentrations of benzaldehyde and of benzalhydrazone (formed by hydrolysis of the azine) did not affect the absorption spectra of the azine at initially low concentrations of azine (less than 0.00002 M), yet nevertheless at the higher concentrations of azine and acid the absorption spectra was affected. A full kinetic investigation, with a view to obtaining confirmation of the suggested mechanism, would not be possible working only with the lower concentrations of azine and acid, as in such conditions the azine would not be wholly converted to the azinium ion, and the absorption of the mixture would then be affected by that of the original azine. Further information about the effect of different concentrations of water on the rate of the reaction would also be required for the full kinetic investigation of the hydrolysis. This would entail the use of a solvent containing less than .00002% water, and would also necessitate the exclusion of all moist air during the filling of the absorption cells, and during the recording of readings on the spectrophotometer.

For these reasons verification of the proposed mechanism for the hydrolysis of benzaldazine hydrochloride was not further investigated.

APPENDIX I.

Definition of Hammett and Deyrup's Acidity Function, Ho.

The acidity function, Ho, (as introduced by Hammett and Deyrup[10]) is an extension of the familiar indicator method of determining hydrogen-ion concentration in dilute aqueous solution, which depends on the colorimetric or spectrometric determination of the indicator ratio, $\frac{C_{BH^+}}{C_B}$, where B represents the indicator and BH^+ its conjugate acid. In dilute solution the reaction:-

$$B + H^+ \rightleftharpoons BH^+$$

obeys the mass law $K_B = \frac{C_{BH^+}}{C_B[H^+]}$ where K_B is the indicator constant.

From this expression, $[H^+] = \frac{C_{BH^+}}{C_B \cdot K_B}$ ..... Equation VI

$$-\log [H^+] = -\log \frac{C_{BH^+}}{C_B \cdot K_B}$$

i.e. $pH = pK_B - \log \frac{C_{BH^+}}{C_B}$ .....Equation VII

In more concentrated acid solution, or in non aqueous solutions, the classical mass law no longer applies, but the ratio, $\frac{C_{BH^+}}{C_B}$, still represents a quantitative measure of the tendency of the solution to donate a proton to a neutral base. In order to provide a common basis for the use of different indicators, dilute aqueous solution is chosen as a reference state and Ho is defined by:-

$$Ho = pK_B - \log \frac{[BH^+]}{[B]}$$ ..... Equation I

where pK_B is still the indicator constant in dilute aqueous solution. Thus Ho = pH in dilute aqueous aqueous solutions. (cf. Equations I and VII).

Equation VI, for non-aqueous or concentrated solutions may be written as:-

$$h = \frac{C_{BH^+}}{C_B \cdot K_B}$$ ..... Equation VIII

where h, although not equal to $[H^+]$, is nevertheless a direct measure of the proton availability.

APPENDIX II.

Derivation of Hammett and Deyrup's equation II.

Hammett and Deyrup's Equation I gave the definition of the acidity function, Ho, of a particular solution. If Ho for a particular solvent can be found then Equation I can be employed to find the indicator constant of a base, provided $\frac{C_{BH^+}}{C_B}$ for that base can be found. One method for determining this indicator ratio is by a spectrometric method. The latter is a general method for obtaining the concentrations of two components in a mixture, when the absorption curves for each component separately and for the mixture are known. Further the total molar concentrations of the two components must be a constant. That is, if a solute exists in two forms, say B and BH^+ so that the total concentration C is equal to the sum of the concentrations of these two forms:-

$$C = C_B + C_{BH^+} \qquad \text{..... Equation IX}$$

and as $$K = -\frac{\log T}{C\,l} \qquad \text{..... Equation X}$$

where K = molecular extinction coefficient

C = concentration

l = length traversed by light through absorption cell

then $$-\log T = (K_B C_B + K_{BH^+}\ C_{BH^+}) \qquad \text{..... Equation XI}$$

provided also each substance absorbs independently of the other.

Equations IX, X and XI can be combined by eliminating $-\frac{\log T}{l}$ from IX and XI, giving

$$K\,C = K_B C_B + K_{BH^+}\,C_{BH^+} \qquad \text{..... Equation XII}$$

Substituting for C in XII, using its value in IX:-

$$K(C_B + C_{BH^+}) = (K_B C_B + K_{BH}\ + C_{BH}\ ) \text{ ..... Equation XIII}$$

$\div$ XI by C_B, $$K + \frac{C_{BH^+}}{C_B} = K_B + \frac{K_{BH^+}\ C_{BH^+}}{C_B}$$

i.e. $$\frac{(C_{BH^+})}{(C_B)} \qquad \frac{(K - K_B)}{(K_{BH^+} - K)} \qquad \text{..... Equation XIV}$$

Thus from Equation XIV $\frac{C_{BH^+}}{C_B}$ can be found if K, K_B and K_{BH^+} are known.

Combining XIV with I gives Equation II,

$$\text{i.e. } pK_B = Ho + \log \frac{(K - K_B)}{(K_{BH^+} - K)}$$

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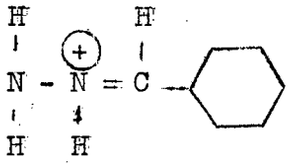
that the reaction was of the first order with respect to the azine concentration. The fact that at high acid concentrations (i.e. greater than 0.3 molar) the curve was no longer completely linear, did not necessarily mean a change in the order of the reaction, but was interpreted (see (a) above) as due to the formation of comparatively high concentrations of the hydrazone of benzaldehyde, the molecular extinctions of which would no longer be negligible. Similarly the shape of the log ε-time curve for the first twelve minutes of reaction was due to the presence of unchanged benzaldazine as well as of benzaldazinium ion.

The effect of different acid concentrations on the rate of the reaction was determined by measuring the rates at different molarities of hydrogen chloride, keeping the azine and the water concentrations the same. In order to obtain the specific velocity constants for the hydrolysis at various acid concentrations, the slopes of the corresponding log ε-time curves were required. Accordingly the curves shown in Figure IX were drawn. These represented the log ε against time curves for solutions of fixed azine concentration, but varying acid concentrations at the wave length of 295 mμ. This choice of wave length out of the five possible ones of 280, 285, 290, 295 and 300 mμ was made, as at the first three mentioned the absorption of the hydrazone of benzaldehyde formed affected the slopes of the log ε-time curves at the higher acid concentrations to a greater extent than at the last two wave lengths. Further 300 mμ was cut out as at this wave length the values of log ε dropped too low after a comparatively short time to fall on the more accurate part of the Beckmann spectrophotometeric scale. An examination of Figure IX showed that only on 0.48, 0.54 and 0.682 molar hydrogen chloride solutions did the log ε-time curves cease to be linear after about eighteen minutes. The specific velocity constants K, were obtained from the linear portions of the curves in Figure IX, from the relationship:-

$$K = \frac{-2.303}{\text{rate of change of log } \varepsilon \text{ with time}} \ \text{min}^{-1}$$

The hydrazone would now react with a solvated proton at the nitrogen atom having the higher electron density, i.e. at the nitrogen atom attached by the double bond to the carbon atom, forming V,



The final conversion of V to benzaldehyde and hydrazine would occur by a similar mechanism to that suggested above for the conversion of II to benzalhydrazone and benzaldehyde.

(4) Attempted preparations of aliphatic aldazinium salts.

(a) Attempted preparations of simple and complex salts of aliphatic azines.

, Attempts were made to prepare both simple and complex salts of acetaldazine, n-butaldazine, n-propaldazine and of crotonaldazine.

The preparation of a hydrochloride of acetaldazine was attempted by passing hydrogen chloride through its ethereal solution. This yielded a white crystalline product, consisting mainly of hydrazine dihydrochloride. All efforts to make the hydrohalides of this azine, if done in the presence of water, gave the corresponding hydrazinium salt. When working under strictly anhydrous conditions (using the apparatus shown in Figure XII, page 37a) oils which failed to crystallise even at -50°C were obtained.

Attempts to make a chloro- or bromo-stannate, a chloro-, bromo-, or iodo-antimonite of acetaldazine using different solvent and widely differing conditions, were equally unsuccessful. If done in the presence of even traces of water hydrazinium salts were precipitated, whereas when carried out in completely anhydrous conditions crystalline products were obtained which showed on analysis that the azine had polymerised in varying degrees.

n-Butaldazine, b.p. 186 - 188°C, was prepared and attempts were