The Action of
Semicarbazide Hydrochloride on the P-quinones.

A

Contribution

to the

Study of Hydroxyazo-bodies.

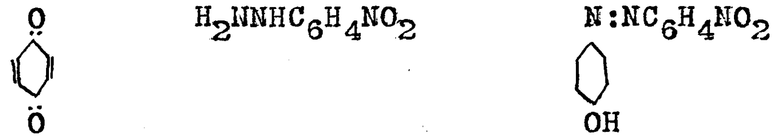
by

James Alexander Russell Henderson, B.Sc..

Contents.

A Contribution to the Study of Hydroxyazo-bodies.

The researches which have been made in recent years with regard to the constitution of "quinone hydrazones" prove conclusively that these bodies under the conditions of examination are not quinone derivatives but hydroxyazo-compounds; where quinone hydrazones might have been expected rearrangement invariably seems to take place with formation of hydroxyazo-bodies. Thus Borsche (Ann.1907, 357,171) found that by condensing o-nitrophenylhydrazine with p-benzoquinone there resulted not the quinone hydrazone but the isomeric hydroxyazo-body:-



The spectroscopic evidence, at any rate for the para-quinones, also supports the view that where quinone hydrazones might be expected hydroxyazo-bodies are formed. Tuck (Trans.1907,91,449) obtained similar curves for benzeneazophenol (quinonehydrazone) and benzeneazophenetole which latter body was proved by Jacobsen and Fischer (Ber.1892,25,995) to be a true azo-derivative, and hence could prove conclusively that the parent substance must have the same constitution as the ester, that is, it is a true azo-compound of the formula $C_6H_5N:NC_6H_4OH$ and not a quinone hydrazone $C_6H_5HN.N:C_6H_4:O$.

The present work was undertaken with a view to examining both by chemical and spectroscopic means the type of compounds obtained by the action of semicarbazide upon the para-quinones.

That a close resemblence should exist between the semicarbazones on the one hand and the hydrazones or phenylhydrazones on the other is evident from the similarity in the constitution of these substances.

$H_2N.NH_2$	$H_2N.NHCONH_2$	$H_2N.NHC_6H_5$
Hydrazine.	Semicarbazide.	Phenylhydrazine.

In semicarbazide an atom of hydrogen has been replaced in the hydrazine molecule by the $-CONH_2$ group and in phenylhydrazine by the $-C_6H_5$ radical.

With aldehydes and ketones the condensation products formed by the action of semicarbazide hydrochloride are very similar to the phenylhydrazones.Many of the latter exist in stereoisomeric forms according to the Hantzsch-Werner theory and recent work on corresponding semicarbazones shows that they also are capable of existence in stereoisomeric forms.(Heilbron and Wilson,Trans. 1912,101,1482).

The results of the present examination prove that the similarity between hydrazone derivatives and semicarbazones extends also to the para-quinone condensation products,for where quinone semicarbazones would have been expected the isomeric hydroxyazoformamide derivatives are invariably formed.

D. Sc.

April. 1913

1) Williamina Abel
2) Jas. A. R. Henderson
3) Alex. S. Russell
4) Geo. H. Edington (2 vols.) ✓

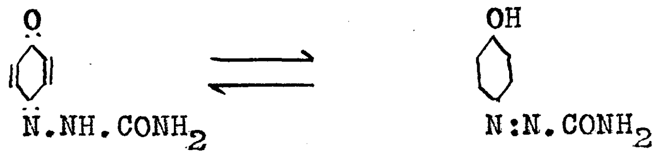
Press Mark :—

Reader's Name :—

No. of Reader's Page :—

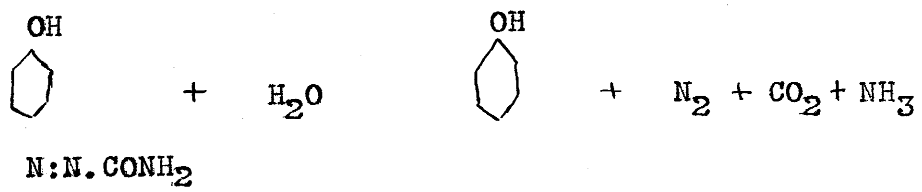
Date :—

These compounds together with their salts and esters have now been carefully examined for a large series of quinones and along with their spectroscopic examination form the subject of the present thesis.The knowledge of the quinone semicarbazones previous to the present work was somewhat meagre.Thiele and Barlow (Ann.1898, 302,315) had found that the compound formed by the action of semicarbazide hydrochloride on p-benzoquinone in the proportions necessary for the formation of a monosemicarbazone reacts either as a semicarbazone (I) or as a 4-hydroxybenzeneazoformamide (II)



I II

They found that by the action of a second molecule of semicarbazide hydrochloride a disemicarbazone could be formed,that is,the compound acts as represented by formula I,but on the other hand they proved that boiling with dilute sodium hydroxide gave rise to phenol,the decomposition taking place according to the equation:-



In the light of this reaction it is apparent that the compound reacts in accordance with formula II,and they concluded that the compound is a tautomeric substance in which a hydrogen atom wanders from the semicarbazone group to the oxygen atom,thus forming hydroxyl, a change which involves an alteration from a quinonoid structure to a benzenoid structure.

Some years later,the question of tautomerism in the "quinone semicarbazones" was reinvestigated by Borsche (Ann.1904,334,143)who prepared some condensation products of the para-quinones with semicarbazide hydrochloride but more particularly with carbamylphenylhydrazone hydrochloride $H_2N.NHCONHC_6H_5HCl$,and showed that such bodies were apparently tautomeric.

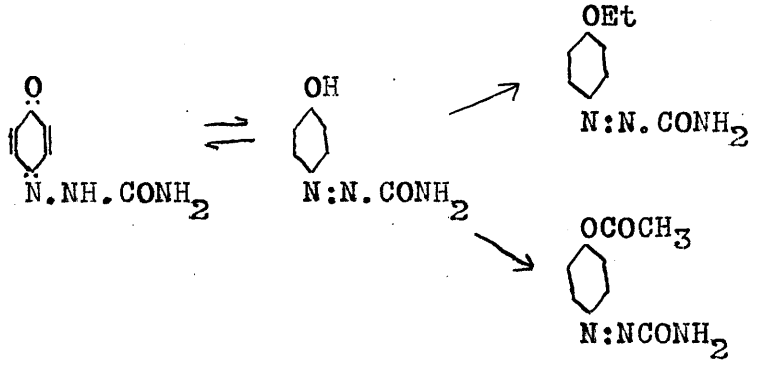
Borsche obtained the compound 4-ethoxybenzeneazoformamide, which from its method of preparation is undoubtedly a true azo-derivative and not a derived semicarbazone,by treatment of p-ethoxyphenylhydrazine with potassium cyanate followed by oxidation of the product with chromic acid mixture:-

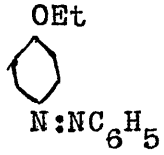
$$H_2N.NHC_6H_4OEt \rightarrow H_2N.CONH.NHC_6H_4OEt \rightarrow H_2N.CON{:}NC_6H_4OEt$$

The author has now prepared this compound directly from 4-hydroxybenzeneazoformamide (quinone semicarbazone) and this shows that the supposed quinone semicarbazone must undoubtedly be tautomeric.

The spectroscopic examination proves most conclusively the azo-constitution of 4-ethoxybenzeneazoformamide,the absorption curve for this substance being practically identical with that obtained by Tuck (loc.cit.) for benzeneazophenetole as shown in Plate I.

The acetyl derivative shows also the same absorption curve and possesses therefore the azo-constitution



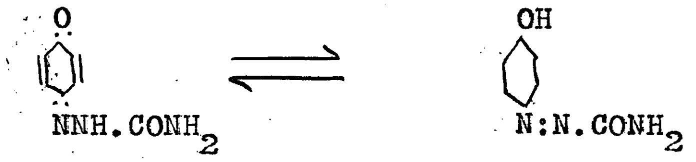


Identical curves.

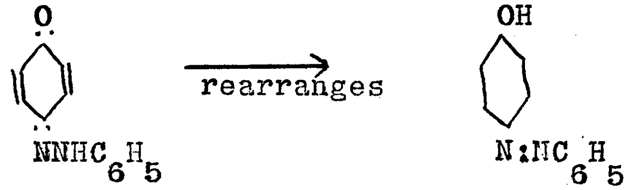
The question as to the constitution of the free mother substance can then be decided by a comparison of its absorption with those of the ethyl and acetyl derivatives,undoubtedly azo-compounds.Plate III shows the curve for the free substance in alcohol, which is identical with that of the ester and hence it must be concluded that under the conditions of examination quinone semicarbazone does not exist as such but rearranges itself to a hydroxyazo-body,a conclusion which is in complete harmony with the similar hydrazones.

That,under special conditions,quinone semicarbazone can exist as such is rendered clear by the fact that a disemicarbazone can be easily obtained,a reaction which could only take place if the monosemicarbazone existed as such.

By analogy the author ventures to suggest that although up to the present the similar quinone hydrazones have evidently only been obtained in their tautomeric forms (azo-bodies) yet it would seem possible that if the proper conditions could be got a quinone hydrazone might exist



(must exist under special conditions) (usual form,stable)

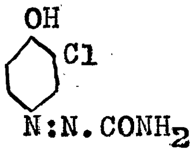


(might exist) (stable)

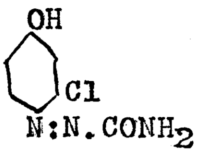
<u>Monochloroquinone and semicarbazide hydrochloride.</u>

When monochloroquinone and semicarbazide hydrochloride react in equimolecular proportions a hydroxyazo-body is formed as is shown by its absorption spectrum and by its behaviour towards alkalis.

When these two substances react it might be expected that each of the two theoretically possible isomerides,I and II,should be formed.In I the hydroxyl radical and the chlorine atom are in the ortho-position and in II they are in the meta-position to one another.



I



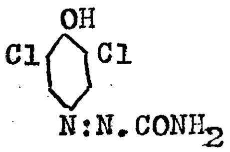
II

Only one compound however could be isolated and that is the compound represented by formula I as is proved in the experimental part by the formation of o-chlorophenol when heated with dilute sodium hydroxide. II should yield m-chlorophenol.

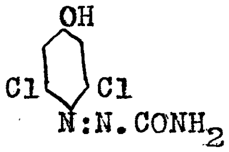
No disemicarbazone could be prepared from monochloroquinone and semicarbazide.

2:6-dichloroquinone and semicarbazide hydrochloride.

When these two compounds react a hydroxyazo-body results and again here only one of the two theoretically possible isomerides Could be isolated.



I



II

Heating with dilute sodium hydroxide gives 2:6-dichlorophenol and not 3:5-dichlorophenol which would result from II.Hence the compound must have the constitution represented by I.

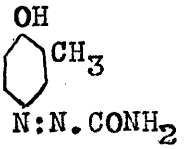
A disemicarbazone could not be obtained.

With 2:5-dichloroquinone and semicarbazide hydrochloride no condensation products could be obtained, and attempts to prepare condensation products of trichloroquinone, tetrachloroquinone and chloranilic acid with semicarbazide hydrochloride were also unsuccessful.

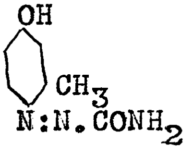
Toluquinone and semicarbazide hydrochloride.

The action of semicarbazide hydrochloride upon toluquinone results in a hydroxyazo-body as in the case of p-benzoquinone.

Theoretically there are two isomerides which might be formed during the reaction since the two oxygen atoms are not spatially the same, - one in which the hydroxyl radical is in the ortho-position to the methyl group (I) and the other in which the hydroxyl and methyl groups are in the meta-position to one another (II)

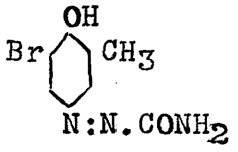


I

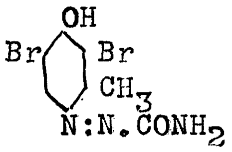


II

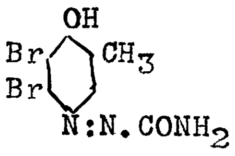
Only one of these two possible isomerides could be isolated and the one obtained is I since the compound yields o-cresol on treatment with dilute sodium hydroxide as described in the experimental part, and not m-cresol as should result from II. Further the bromination of I should give first a monobromo-derivative III in which the bromine atom replaces the hydrogen atom adjacent to the hydroxyl; in II there are two hydrogen atoms in the ortho-position to the hydroxyl and these should be replaced on bromination yielding a dibromo-derivative **IV**, corresponding to the dibromo-derivative of 4-hydroxybenzeneazoformamide.



III

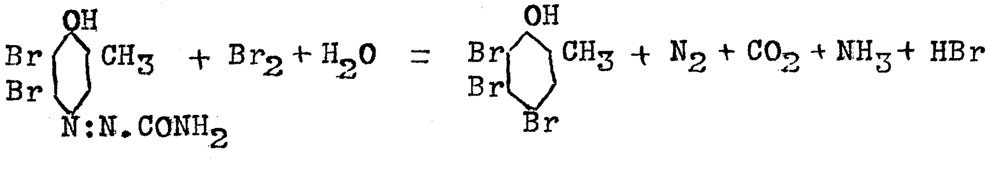


IV



V

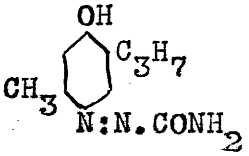
It has been found that a monobromo-derivative is easily formed. Evidence was obtained that **III** might brominate still further and give a dibromo-derivative V. Analysis of the product with excess of bromine showed that it consisted of a mixture of bromination products. The fact of getting from the filtrate a compound containing bromine and melting at 78-79° which corresponds with 1-methyl-2-hydroxy-3:4:5-tribromobenzene which melts at 79° points to the same conclusion :-

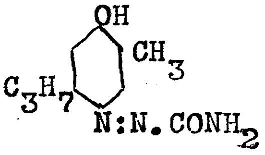


By acting upon the mono-condensation product with a second molecule of semicarbazide hydrochloride, the disemicarbazone of toluquinone is easily prepared thus proving as in the case of the benzoquinone mono-condensation product that it can act tautomerically.

Thymoquinone and semicarbazide hydrochloride.

Here again there are two theoretically possible isomerides (I and II) which might be formed by the reaction of thymoquinone and semicarbazide hydrochloride in equimolecular quantities;one in which the isopropyl radical is in the ortho-position to the hydroxyl group and the other in which the methyl radical occupies this position.


I


II

Only one could be isolated and the formation of thymol by the action of dilute sodium hydroxide proves that the hydroxyazo-compound has the constitution I.(See experimental part).

The hydroxyazo-compound brominates readily and forms first a monobromo-derivative and secondly a dibromo-derivative but whether the second bromine atom enters the nucleus or the side chain could not be decided.That it enters the side chain is probable from the fact that although various experiments were tried it was found impossible to prepare a condensation product from dibromothymoquinone and semicarbazide hydrochloride.

In the case of toluquinone and of the chlorinated benzoquinones (when reaction does take place) only one of the two theoretically possible isomerides could be isolated and in each case the azoformamide group is attached to the benzene nucleus remote from the substituents;and in the case of thymoquinone this group is adjacent to the methyl in preference to the isopropyl radical.From benzoquinone and toluquinone disemicarbazones could be formed;with monochloroquinone,2:6-dichloroquinone and thymoquinone only one molecule of semicarbazide reacts; and with 2:5-dichloroquinone,trichloroquinone,chloranilic acid and dibromothymoquinone no reaction could be observed.

Kehrmann (Ber.1888.21,3315) found a similar state of affairs when studying the action of hydroxylamine upon the substituted quinones,and Staudinger ("Die Ketene"pp.61-70) observed the same phenomena in the case of the action of diphenylketen on the substituted quinones.Whether this inactivity of the substituted quinones is due to steric hindrance or not remains at present unproved but the inactivity is evidently general for a large series of various condensation products as is shown in the present case.

Properties of the hydroxyazoformamides.

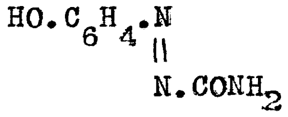
The hydroxyazoformamides are generally yellow crystalline solids easily soluble in alcohol,acetone and glacial acetic acid, slightly soluble soluble in water,and with a few exceptions insoluble in chloroform;all are insoluble in ether,benzene,petroleum ether and carbon disulphide.On treatment with the necessary quantity of sodium hydroxide they form red coloured salts, while when boiled with excess of alkali they are decomposed into the corresponding phenol.

Colour isomerism.

In two cases - benzoquinone and 2:6-dichloroquinone - red forms of the condensation product were obtained in addition to the yellow variety. The origin of this difference of colour is doubtful. It may be due to dimorphism or it may be chemical.

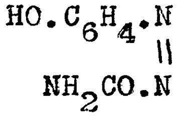
The following possibilities are put forward without further discussion as at present the point cannot be definitely decided.

I. The difference in colour may be due to stereoisomerism in which case the two forms would be syn- and anti-compounds.



$$\begin{array}{l}\mathrm{HO.C_6H_4.N}\\ \qquad\quad\;\;\|\\ \qquad\quad\;\mathrm{N.CONH_2}\end{array}$$

Anti-



$$\begin{array}{r}\mathrm{HO.C_6H_4.N}\\ \|\\ \mathrm{NH_2CO.N}\end{array}$$

Syn-

II. Or the difference may be due to structural isomerism, one form being a hydroxyazo-body and the other a semicarbazone (solid state only).

$\mathrm{HO.C_6H_4.N{:}N.CONH_2}$ $\mathrm{O{:}C_6H_4{:}N.NH.CONH_2}$

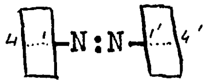
III. The difference of colour may be due to dimorphism.

In solution however both forms are identical and exhibit the characteristic absorption of azo-bodies.

Baly and Tuck (Trans.1906,89,902) state that the origin of colour in azobenzene is due to the grouping  and that the band in the absorption spectrum of this compound is of the same type as the bands in the case of the quinones.

They argue that the origin of the colour is to be found in the vibration of the two benzene nuclei and that this vibration takes place between two extreme forms a and b :-

a



b

" In the form a the four carbon atoms 1,4,1' and 4' are unsaturated and we therefore have an unsaturated carbon atom on each side of the unsaturated nitrogen atoms,thus $\underset{\vdots}{C}.N:N.\underset{\vdots}{C}$ if the unsaturated affinities of the carbon atoms be expressed by dotted lines.It appears that in these circumstances oscillation between the unsaturated affinities is set up,a process which should be included under the term isorropesis".

Crymble,Stewart and Wright (Ber.1910,43,1188) critise the above explanation as to the origin of colour and the band in the visible spectrum.They compare azobenzene and stilbene:-

$C_6H_5.N{:}N.C_6H_5$ azobenzene

$C_6H_5.CH{:}CH.C_6H_5$ stilbene

In azobenzene there is a phenyl group on each side of the unsaturated group -N:N- and in stilbene the two phenyl radicals are separated by the unsaturated group -CH:CH- . There is a close structural analogy between the two compounds.If the explanation given by Baly and Tuck for the band in the visible spectrum in the case of azobenzene is accepted we should expect a similar band in the case of stilbene.But when the spectrum of stilbene is examined it is found that there is no such band in the visible spectrum.

Now all compounds containing the group -N:N- are coloured, e.g. diazomethane is a yellow liquid of low boiling point,and the compounds described in this investigation are of the type

$$RO.C_6H_4.N{:}N.CONH_2$$

(where R is H,Et or acetyl) and are yellow (or red). No vibrations of the nature supposed by Baly and Tuck are possible in these compounds so that it must be concluded that the colour is due solely to the presence of the group -N:N- .If this group is reduced the colour is destroyed;thus 4-ethoxybenzeneazoformamide $EtO.C_6H_4.N{:}N.CONH_2$ is orange-red but 4-ethoxybenzenehydrazoformamide $EtO.C_6H_4.NH.NH.CONH_2$ is colourless as Borsche states (Ann.1904, 334,185).

CONCLUSIONS.

1) The compounds formed by the action of equimolecular proportions of p-quinones and semicarbazide hydrochloride are not semicarbazones but hydroxyazo-compounds. This is proved by their absorption spectra being of the type of true azo-bodies and by their behaviour towards alkali.

2) Quinone semicarbazones must, however, be formed under certain conditions as is shown by the formation of certain disemicarbazones.

3) Quinone hydrazones might exist under certain conditions.

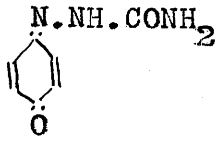
4) The position isomerides which are theoretically possible cannot be prepared owing to "steric hindrance".

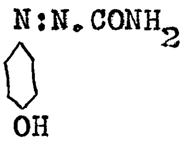
EXPERIMENTAL.

Preparation of the Hydroxyazoformamides and their Salts.

Preparation of p-benzoquinonesemicarbazone.

4-hydroxybenzeneazoformamide.





This compound was prepared by Thiele and Barlow (Ann.1898,302 315) who,by acting on a boiling solution of p-benzoquinone in alcohol with aqueous semicarbazide hydrochloride,obtained a mixture of the mono- and the di-semicarbazones of p-benzoquinone.Borsche (Ann. 1904,334,175) by working with solutions at the room temperature obtained only the mono-derivative.

On repeating the preparation as described by Borsche it was found that a small quantity of the disemicarbazone was invariably formed;this formation of the disenicarbazone can be avoided by carrying out the operation in ice cold solutions.The colour of the product obtained in different experiments varied; sometimes a pure yellow product was obtained,and at others a mixture of red and yellow substances was precipitated,although the conditions of the experiment were apparently the same in every case.

Yellow form.

The pure yellow variety is prepared by dissolving the substance in hot water and cooling rapidly;or by dissolving in acetone and precipitating with carbon disulphide,petroleum ether or benzene in the cold.In these ways minute yellow crystals (needles) were obtained which melt with decomposition at 165-166°.

0.1506 gm.gave 31.9 c.c. of moist nitrogen at 12° C.and 765 mm.

25.31 % nitrogen.

$C_7H_7O_2N_3$ requires 25.45 % nitrogen.

Red form.

The pure red form is obtained by slow cooling of a hot aqueous olution of the yellow form;or by precipitating a hot solution in acetone by hot benzene.It forms little red needles which melt with decomposition.at 165-166°.

0.1580 gm. gave 33.5 c.c.of nitrogen at 12° and 765 mm.

25.33 % nitrogen.

$C_7H_7O_2N_3$ requires 25.45 % nitrogen.

Both forms are equally soluble in water,alcohol,acetone and glacial acetic acid giving reddish-yellow solutions;the two varieties are insoluble in ether,petroleum ether,carbon disulphide,chloro form and benzene.

If the two forms are isomerides the change from one form into the other must take place at the melting point.Prolonged heating of the two varieties in the air oven at 120° causes no change in the colours of the two forms; and no change of colour could be observed in the neighbourhood of their melting point.

Decomposition point.

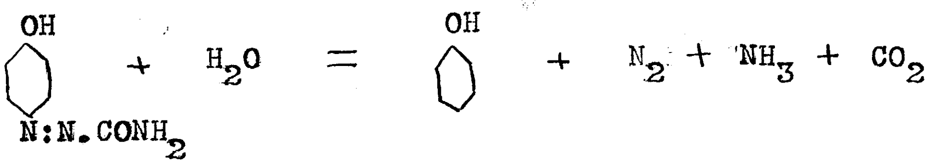
Thiele and Barlow (loc.cit.) state that the substance melts with decomposition at 172° while Borsche (loc.cit.) gives

178° for the melting point. If the temperature is kept at 165-166° the substance melts with decomposition but if rapidly heated it melts and decomposes at any temperature up to 180°.

It is well known that in the case of bodies melting with decomposition, the melting point depends upon the rate of heating.

Action of sodium hydroxide.

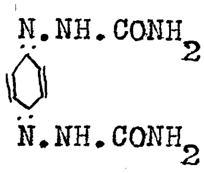
When either the red or the yellow variety of 4-hydroxybenzene azoformamide is boiled with dilute sodium hydroxide ammonia is given off; when dilute sulphuric acid is added to neutralise the solution carbon dioxide is evolved and phenol is formed at the same time. The following equation represents the reaction:-



This shows that the substance exists in the form of a hydroxyazo-compound and the same conclusion is arrived at from the consideration of the absorption spectrum (Plate III). That is an atom of hydrogen has wandered from the semicarbazone group to the oxygen atom with the formation of hydroxyl.

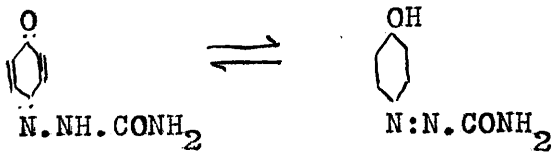
P-benzoquinone and two molecules of semicarbazide hydrochloride.

Preparation of p-benzoquinonedisemicarbazone.

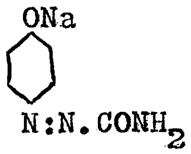


The product obtained by heating on the water bath a mixture of p-benzoquinone in alcohol and an aqueous solution of two molecules of semicarbazide hydrochloride is dark red and melts with decomposition at 243°.It is insoluble in most organic solvents but dissolves in sodium hydroxide.This agrees with what Thiele and Barlow found (loc.cit.).The same compound is also formed by heating equimolecular proportions of 4-hydroxybenzeneazoformamide and semicarbazide hydrochloride.

This reaction shows that the parent substance can act tautomerically.



Sodium salt of 4-hydroxybenzeneazoformamide.



When 4-hydroxybenzeneazoformamide is dissolved in sodium hydroxide a deep red solution is formed.

Evidently the sodium salt is formed.In order to isolate the sodium salt the following method was used. The parent substance was dissolved in acetone and alcoholic sodium ethoxide added in slight excess. By addition of petroleum the sodium salt was precipitated and after standing overnight was filtered off and washed with petroleum ether. In order to purify the salt it was dissolved in acetone and after filtering from sodium ethoxide was reprecipitated by the addition of petroleum ether. After two repetitions of this process the sodium salt was obtained pure.

It forms minute red crystals soluble in water, alcohol and acetone giving red solutions; it is insoluble in ether, chloroform, benzene and petroleum ether. With dilute acids the salt is decomposed with regeneration of the yellow form of 4-hydroxybenzeneazoformamide.

0.3472 gm. gave 0.1304 gm. of sodium sulphate.

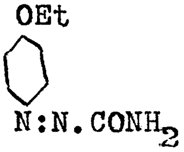
12.16 % sodium $C_7H_6O_2N_3Na$ requires 12.39 % sodium.

Silver salt.

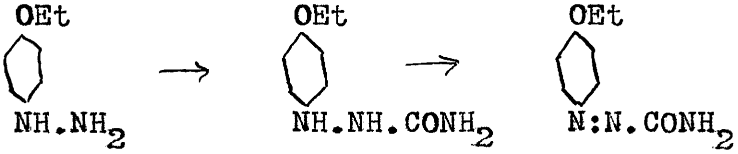
$\mathrm{AgO \cdot C_6H_4 \cdot N{:}N{\cdot}CONH_2}$

When aqueous silver nitrate was added to a solution of the sodium salt in water, a ruby red precipitate was formed which was filtered off and washed with water, alcohol and ether. When dry the silver salt is obtained as a fine red powder which explodes when heated. It is soluble in ammonium hydroxide and in pyridine forming yellow solutions.

Preparation of 4-ethoxybenzeneazoformamide.



Borsche (Ann. 1904, 334, 185) prepared the ethyl ether of 4-hydroxybenzeneazoformamide from p-ethoxyphenylhydrazine by the action of potassium cyanate followed by oxidising the p-ethoxybenzenehydrazoformamide formed, with chromic acid mixture:-



From his method of preparation it is evident that there is no possibility of any semicarbazone being formed and the substance must be an azo-body. He gives the melting point as 164-165° with decomposition.

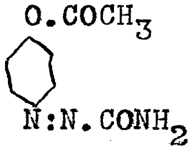
This compound has now been prepared directly by Purdie's alkylation method. (Purdie and Pitkeathly, Trans. 1899, 75, 153). 3 grams of 4-hydroxybenzeneazoformamide were dissolved in acetone and heated with 4 grams of silver oxide and 6 grams of ethyl iodide for several hours on a water bath under a reflux condenser. After recovering the silver iodide by filtration and distilling off the acetone the ethyl ether was left which after repeated crystallisations from methyl alcohol was obtained pure.

The ether forms beautiful orange red leaflets soluble in water,alcohol and acetone but insoluble in chloroform,benzene and petroleum ether.It melts with decomposition at 162°.

0.11 gm.gave 21.1 c.c. of nitrogen at 19.5° and 759 mm.

21.89 % nitrogen. $C_9H_{11}O_2N_3$ requires 21.76 % nitrogen.

Preparation of 4-acetoxybenzeneazoformamide.



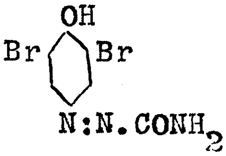
4 grams of 4-hydroxybenzeneazoformamide were dissolved in absolute alcohol and to the solution were added 0.6 gram of sodium dissolved in absolute alcohol and 4 grams of acetyl chloride.After standing for an hour the precipitated sodium chloride was filtered off and the filtrate allowed to evaporate.The residue after recrystallisation from alcohol formed beautiful orange red crystals which melt with decomposition at 158°.

4-acetoxybenzeneazoformamide is soluble in water from which it crystallises out in orange red needles,alcohol (plates or needles) chloroform (plates),acetone,glacial acetic acid;slightly soluble in carbon tetrachloride and ether;insoluble in carbon disulphide and petroleum ether.

0.1496 gm.gave 26.8 c.c. of nitrogen at 20° and 756 mm. 20.38 % of nitrogen. $C_9H_9O_3N_3$ requires 20.29 % nitrogen.

Bromination of 4-hydroxybenzeneazoformamide.

Preparation of 4-hydroxy-3:5-dibromobenzeneazoformamide.



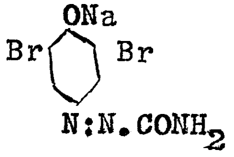
Borsche prepared this compound (m.p.223-225°) by brominating 4-hydroxybenzeneazoformamide.(Ann.1904,334,175)

2 grams of 4-hydroxybenzeneazoformamide and 6 grams of sodium acetate were dissolved in 60 c.c. of glacial acetic acid and cooled in ice water; 4 grams of bromine dissolved in 40 c.c..of glacial acetic acid were then added slowly from a dropping funnel.Towards the end of the addition of the bromine a yellow precipitate began to form.After allowing to stand overnight the precipitate was filtered off and washed with a little alcohol.The substance was purified by crystallising from glacial acetic acid and water.

The compound is obtained in yellow needles soluble in acetone and glacial acetic acid,slightly soluble in alcohol and water,insoluble in petroleum ether,ether,chloroform and benzene.It melts with decomposition at 223-225°.

Borsche states (loc.cit.) that,on the addition of water to the mother liquors from the reaction mixture,white crystals of tribromophenol are obtained.On attempting to repeat this it was found that water gave a further quantity of 4-hydroxy-3:5-dibromobenzeneazoformamide This difference is probably due to the difference of temperature at which bromination was carried out.The above reaction was done in ice cold solution while Borsche brominated at the room temperature.

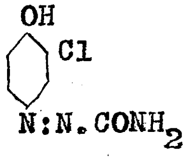
Sodium salt.



A small quantity of this salt was prepared by adding sodium ethoxide to an acetone solution of the parent substance.The salt was precipitated by petroleum ether and purified by dissolving in acetone,filtering and reprecipitating with petroleum ether.

The salt is obtained in red needles which are soluble in water,alcohol and acetone giving red solutions;it is insoluble in chloroform,ether and petroleum ether.

Preparation of 4-hydroxy-3-monochlorobenzeneazoformamide.



Monochlorobenzoquinone was prepared according to the method of Levy and Schultz (Ann.1881,210,138,145) by passing dry hydrogen chloride into a chloroform solution of quinol in order to form mono chloroquinol and then oxidising the latter compound with chromic acid mixture.

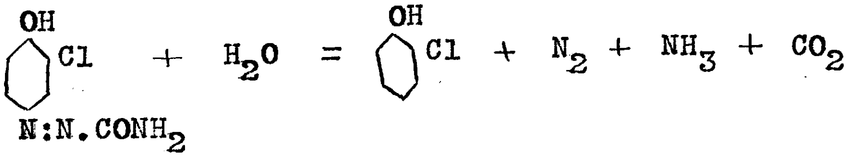
In order to prepare 4-hydroxy-3-monochlorobenzeneazoformamide (not previously described) 7 grams of monochlorobenzoquinone were dissolved in alcohol and after cooling in the ice chest were mixed with a solution of 5.5 grams of semicarbazide hydrochloride in water. 7.8 grams of a yellowish brown precipitate soon settled out. This precipitate was filtered off and washed with a little water. From the mother liquors 0.7 gram of the product was obtained on slow evaporation.

In order to purify the product it was dissolved in acetone, filtered and precipitated with petroleum ether.In this way minute brownish yellow crystals were obtained which melted with decomposition at 185°.

The substance is soluble in water,alcohol,acetone and glacial acetic acid;insoluble in chloroform,benzene,carbon disulphide and petroleum ether.

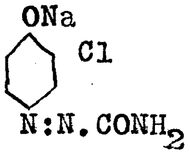
0.1518 gm.gave 27.4 c.c. of nitrogen at 17° and 760 mm.

20.96 % nitrogen. $C_7H_6O_2N_3Cl$ requires 21.05 % nitrogen. When the substance is boiled with dilute sodium hydroxide it evo evolves ammonia and gives a product with the characteristic smell of a chlorinated phenol.After neutralising with dilute sulphuric acid,extracting with ether,drying and removing the ether,a liquid was left which boiled at 175° thus proving it to be o-chlorophenol which boils at 176°.The decomposition takes place according to the equation:-



The production of o-chlorophenol by the action of sodium hydroxide shows that the semicarbazide hydrochloride attacks the oxygen atom remote from the chlorine atom.

Sodium salt of 4-hydroxy-3-monochlorobenzeneazoformamide.



The sodium salt was prepared by dissolving 4-hydroxy-3-monochlorobenzeneazoformamide in acetone and making the solution alkaline with sodium ethoxide.On addition of petroleum ether the sodium salt was precipitated and purified by dissolving in acetone,filtering the solution and reprecipitating with petroleum ether.

The salt thus obtained has a dark red colour and is soluble in water,alcohol and acetone but insoluble in petroleum ether, benzene,chloroform and carbon disulphide.Dilute acids regenerate the free parent substance.

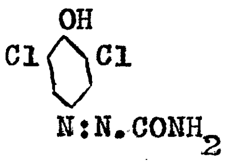
0.2734 gm.gave 0.0865 gm.of sodium sulphate. 10.25 % sodium.

$C_7H_5O_2N_3ClNa$ requires 10.38 % sodium.

Attempt to prepare a disemicarbazone of monochlorobenzoquinone.

A mixture of one molecule of monochlorobenzoquinone in alcohol and two molecules of semicarbazide hydrochloride in water was heated on the water bath for some time.A brownish yellow product was obtained which after filtering off,washing with water and drying melted with decomposition at 185°;this shows that the product is identical with 4-hydroxy-3-monochlorobenzeneazoformamide and not a disemicarbazone.

Preparation of 4-hydroxy-3:5-dichlorobenzeneazoformamide.



2:6-dichlorobenzoquinone was prepared according to the method of Faust (Ann.1868,149,153) by adding trichlorophenol to well cooled fuming nitric acid.

8.8 grams of 2:6-dichlorobenzoquinone were dissolved in 200 c.c. of alcohol and to the well cooled solution,a cold solution of 5.5 grams of semicarbazide hydrochloride in 30 c.c. of water was added and the mixture left in the ice chest overnight.An orange red precipitate formed which was filtered off and washed with water On examining the product with a lens it was seen to consist of a mixture of red and yellow needles with the red predominating.The substance was purified by dissolving in acetone,filtering the solution and then adding petroleum ether to precipitate the 4-hydroxy-3:5-dichlorobenzeneazoformamide.In this way the substance was obtained as a yellow precipitate which consisted of minute needles. By allowing an acetone solution to evaporate slowly little yellow needles were obtained which melted with decomposition at 218°.

The product so obtained is soluble in water,alcohol,acetone and glacial acetic acid giving reddish yellow solutions;it is insoluble in chloroform,benzene,ether,petroleum ether and carbon disulphide.

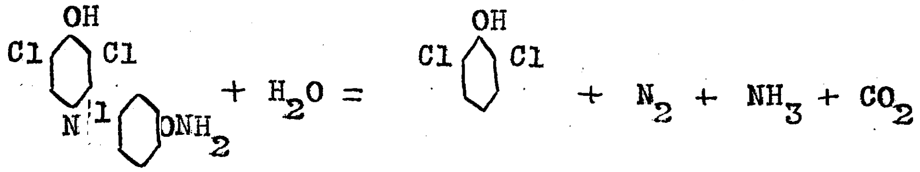
Although the same methods were employed as were successful in the case of 4-hydroxybenzeneazoformamide the red form could not again be obtained as from all solvents only the yellow form crystallised out.

0.1508 gm. gave 22.5 c.c. of nitrogen at 15° and 761 mm.

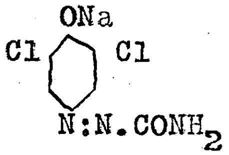
17.79 % nitrogen. $C_7H_5O_2N_3Cl_2$ requires 17.95 % nitrogen.

Action of sodium hydroxide on 4-hydroxy-3:5-dichlorobenzeneazoformamide.

When the substance is boiled with dilute sodium hydroxide ammonia is given off;after neutralising the liquid with dilute sulphuric acid,it was extracted with ether and the extract dried over calcium chloride.On distilling off the ether a residue was left which had the characteristic smell of a chlorinated phenol.After recrystallisation from ether white crystals were obtained which melted at 63°. Beilstein,Vol.II,670,gives the melting point of 2:6-dichlorophenol as 65° and Watt's Dictionary of Chemistry (latest Edition) as 63°. The decomposition takes place according to the equation :-



Sodium salt of 4-hydroxy-3:5-dichlorobenzeneazoformamide.



An alcoholic solution of sodium ethoxide was added to an acetone solution of 4-hydroxy-3:5-dichlorobenzeneazoformamide until the mixture gave an alkaline reaction.Petroleum ether precipitated a dark orange red substance which was purified in the usual way.

The substance so obtained is dark orange red in colour and dissolves in water,alcohol and acetone forming red solutions;it is insoluble in ether,benzene,chloroform,petroleum ether and carbon disulphide.

0.2010 gm. gave 0.055 gm. of sodium sulphate, sodium 8.86 %.

$C_7H_4O_2N_3Cl_2Na$ requires 8.98 % sodium.

2:6-dichlorobenzoquinone and two molecules of semicarbazide hydrochloride.

An attempt to prepare a disemicarbazone was unsuccessful. After the reaction mixture had been heated on the water bath for some time a red precipitate formed and this after standing some hours was filtered off,washed with water and dried.The substance obtained melted with decomposition at 218° and was thus proved to b be 4-hydroxy-3:5-dichlorobenzeneazoformamide and not a disemicarbazone. The red product when dissolved in acetone gave a reddish yellow solution from which petroleum ether precipitated the yellow variety.

2:5-dichlorobenzoquinone and semicarbazide hydrochloride.

2:5-dichlorobenzoquinone was prepared according to the method of Ling (Trans.1892,61,558) by treating quinol with potassium chlorate and hydrochloric acid and subsequent oxidation of the p-dichloroquinol with chromic acid mixture.

1.5 grams of 2:5-dichlorobenzoquinone were dissolved in alcohol and 1.3 grams of semicarbazide hydrochloride dissolved in water added.After standing an hour a yellow product had separated.This was filtered off,washed with water and dried.It melted without decomposition at 161°.By taking a melting point of the precipitate mixed with 2:5-dichlorobenzoquinone it was proved that the yellow precipitate was unchanged 2:5-dichlorobenzoquinone.

The following method was also tried. 1.5 grams of 2:5-dichlorobenzoquinone were dissolved in alcohol and treated with an aqueous solution of 1.3 grams of semicarbazide hydrochloride and 2 c.c. of 5 N sodium hydroxide added.As in the preceeding case the precipitate consisted of 2:5-dichlorobenzoquinone.

Although other methods were tried the result was a negative one in every case.

Trichlorobenzoquinone and semicarbazide hydrochloride.

2 grams of trichlorobenzoquinone obtained from Kahlbaum were dissolved in alcohol and treated with an aqueous solution of 1 gram of semicarbazide hydrochloride.The precipitate obtained was unchanged trichlorobenzoquinone.Other methods were attempted but with a like negative result.

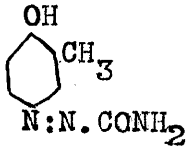
Tetrachlorobenzoquinone and semicarbazide hydrochloride.

2 grams of tetrachlorobenzoquinone obtained were dissolved in alcohol and treated with an aqueous solution of 1 gram of semicarbazide hydrochloride.The precipitate which formed after some time was proved to be unchanged tetrachlorobenzoquinone by the fact that it sublimed completely without melting.

Chloranilic acid and semicarbazide hydrochloride.

No reaction between these two compounds could be obtained.

Preparation of 3-methyl-4-hydroxybenzeneazoformamide.



Toluquinone was prepared by the method of Schnitzer (Ber.1887 20,2283) by oxidising o-toluidine with potassium dichromate and sulphuric acid.

18 grams of toluquinone were dissolved in 250 c.c. of alcohol and after cooling in the ice chest were mixed with a cold solution of 16 grams of semicarbazide hydrochloride in water. A dense yellow precipitate formed in a few minutes,which after standing in the ice chest for an hour was filtered off,washed with a little water and d dried. On allowing the mother liquors to evaporate slowly more of the substance was obtained.Total weight of the condensation product was 22.5 grams.The product was purified by dissolving in boiling alcohol,filtering the solution and allowing it to cool slowly.

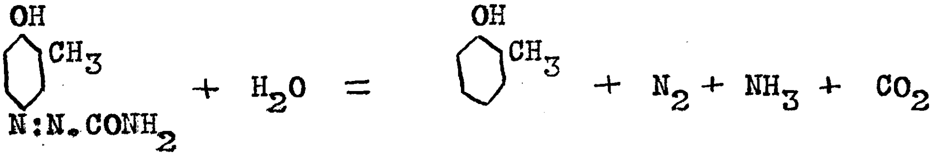
Minute yellow needles were thus obtained which melt with decomposition at 178-179°.The substance is soluble in alcohol,water, acetone and glacial acetic acid forming yellow solutions.It is very slightly soluble in chloroform and insoluble in benzene,ether,petroleum ether and carbon disulphide.

0.155 gm.gave 31.1 c.c. of nitrogen at 16° and 759 mm.

23.38 % nitrogen. $C_8H_9O_2N_3$ requires 23.46 % of nitrogen.

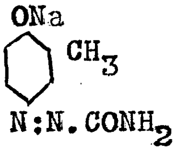
Action of sodium hydroxide on 3-methyl-4-hydroxybenzeneazoformamide

When the substance was dissolved in dilute sodium hydroxide it gave a red solution which on boiling evolved ammonia;after neutralising with dilute sulphuric acid the solution was extracted with ether.The solid residue obtained from the extract was crystallised from ether and obtained in white crystals which melted at 30° and gave a picrate melting at 86°.O-cresol melts at 30° and its picrate at 88°. The decomposition takes place according to the equation:-



This reaction shows that the semicarbazide attacks the oxygen remote from the methyl radical.

Sodium salt of 3-methyl-4-hydroxybenzeneazoformamide.

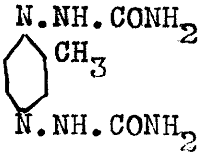


The salt was prepared in the usual way.It is dark red in colour and dissolves in water,alcohol and acetone forming red solutions.It is insoluble in chloroform,benzene,ether and petroleum ether.

.3521 gm. gave .1227 gm. of sodium sulphate, 11.28 % sodium.

$C_8H_8O_2N_3Na$ requires 11.44 % sodium.

Preparation of toluquinonedisemicarbazone.



0.6 gram of 3-methyl-4-hydroxybenzeneazoformamide was dissolved in alcohol and to the boiling solution 0.33 gram of semicarbazide hydrochloride dissolved in water was added,and the mixture heated on the water bath for an hour.An orange precipitate began to form.After cooling and allowing to stand overnight the product was filtered off,washed with water and dried.The disemicarbazone melts with decomposition at 240°.

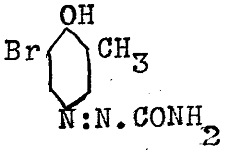
0.1218 gm.gave 36.5 c.c. of nitrogen at 13° and 760 mm.

35.42 % nitrogen. $C_9H_{12}O_2N_6$ requires 35.59 % nitrogen.

It is evident from the formation of a disemicarbazone that 3-methyl-4-hydroxybenzeneazoformamide acts as a hydrazone towards semicarbazide hydrochloride although it behaves as an azo-body towards alkali.(Compare benzoquinone.)

Action of bromine on 3-methyl-4-hydroxybenzeneazoformamide.

I. With one equivalent of bromine.Preparation of 3-methyl-4-hydroxy-5-monobromobenzeneazoformamide.



4 grams of 3-methyl-4-hydroxybenzeneazoformamide were dissolved in 100 c.c. of glacial acetic acid and 12 grams of sodium acetate added;then 1 c.c. of bromine dissolved in 50 c.c. of glaciaial acetic acid was slowly added to the well cooled solution.After allowing to stand for an hour the mixture was treated with a little water.A yellow precipitate separated out which was filtered off and washed with water,alcohol and petroleum ether.After repeated crystallisations from boiling alcohol the compound was obtained in little yellow needles which melted with decomposition at 205°.It is soluble in water,alcohol,acetone and glacial acetic acid;insoluble in benzene,carbon disulphide,ether,chloroform and petroleum ether.Sodium hydroxide dissolves the compound forming a deep red solution;evidently a sodium salt is formed.

0.1394 gm.gave 20 c.c. of nitrogen at 19° and 755 mm.

16.39 % nitrogen. $C_8H_8O_2N_3Br$ requires 16.28 % nitrogen.

By analogy the bromine atom probably enters the ring in the ortho-position to the hydroxyl as Borsche (loc.cit) found that brominating 3-methyl-4-hydroxybenzeneazoformanilide gave the same product as was formed by the action of phenylsemicarbazide hydrochloride on 3-bromotoluquinone,i.e. the bromine goes into the ring adjacent to the hydroxyl. This is also to be expected from the behaviour of phenols when brominated.

II. With excess of bromine.

4 grams of 3-methyl-4-hydroxybenzeneazoformamide were dissolved in glacial acetic acid and 12 grams of sodium acetate added. To the solution cooled with ice water excess of bromine in glacial acetic acid was slowly added. A yellow precipitate formed which after repeated crystallisations from alchol formed yellow needles which melted not sharply about 225-228°. Analysis of the crystals showed that the product was a mixture.

1) 0.1483 gm. gave 19 c.c. of nitrogen at 19° and 755 mm.
   14.9 % nitrogen.

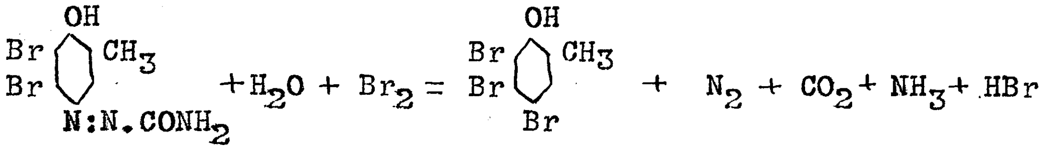
2) 0.1528 gm. gave 20.2 c.c. of nitrogen at 20° and 756 mm.
   15.04 % nitrogen.

$C_8H_9O_2N_3$	requires	23.46 % nitrogen	I
$C_8H_8O_2N_3Br$	requires	16.28 % nitrogen	II
$C_8H_7O_2N_3Br_2$	requires	12.46 % nitrogen	III

The melting point of the product with excess of bromine points to the formation of a considerable amount of the dibromo-derivative. I melts at 178-179°, II at 205° and III should melt between 230° and 240° judging by the increase in the case of 4-hydroxy benzeneazoformamide and its monochloro- and dichloro-derivatives and in the case of 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide and its monobromo- and dibromo-derivatives. (See Table I).

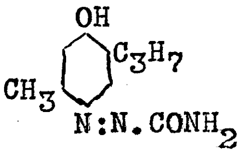
The quantity of material on hand did not allow of further investigation.

The filtrate from the bromination product gave a white precipitate with much water. After filtering off the precipitate and crystallising repeatedly from dilute alcohol white needles were obtained which melted at 78-79°. This substance is evidently 1-methyl-2-hydroxy-3:4:5-tribromobenzene which melts at 79°. The following equation shows how it might be formed:-



Action of semicarbazide hydrochloride on thymoquinone.

Preparation of 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide.



Thymoquinone was prepared from thymol by first converting it into 6-nitrosothymol by Klages' method (Ber. 1899, 32, 1518); the 6-nitrosothymol was changed into thymoquinone by reduction to 6-amino thymol and subsequent oxidation to thymoquinone according to the method of Liebermann and Ilinski. (Ber. 1885, 18, 3194). Compare Henderson and Sutherland (Trans. 1910, 97, 1617).

8 grams of thymoquinone were dissolved in alcohol and to the well cooled solution a cold aqueous solution of 4 grams of semicarbazide was added. A yellow precipitate began to form at once. After

the mixture had been allowed to stand in the ice chest for some hours the precipitate was filtered off,washed and dried.By crystallising from boiling alcohol the substance was obtained pure in the form of microscopic yellow needles which melted with decomposition at 201-202°.

The substance is soluble in water,alcohol,acetone and glacial acetic acid;slightly soluble in chloroform;insoluble in benzene, ether,petroleum ether and carbon disulphide.

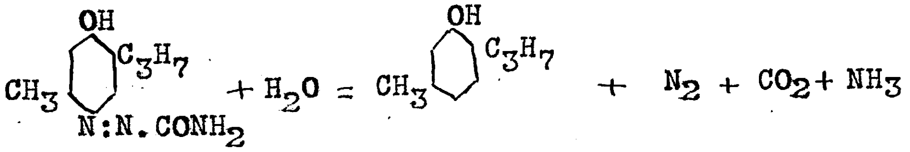
0.1504 gm. gave 25 c.c. of nitrogen at 18° and 754 mm.

19.04 % nitrogen. $C_{11}H_{15}O_2N_3$ requires 19 % nitrogen.

Action of sodium hydroxide.

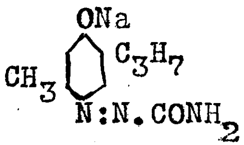
When 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide is boiled with dilute soduium hydroxide thymol is formed as was proved by working up the reaction product in the usual way.The extract obtained had the characteristic smell of thymol and boiled at 130°. Thymol boils at 131°.

The decomposition takes place according to the equation:-



This decomposition shows that the semicarbazide attacks the oxygen atom in thymoquinone adjacent to the methyl group and remote from the isopropyl radical.

Sodium salt of 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide.



The sodium salt was prepared in the usual way and obtained in large ruby red crystals (needles) which are soluble in water,alcohol and acetone forming red solutions;insoluble in chloroform,ether, benzene,petroleum ether and carbon disulphide.

0.3552 gm. gave 0.1052 gm.of sodium sulphate.

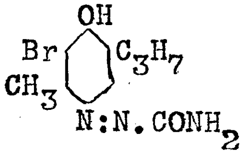
9.59 % sodium. $C_{11}H_{14}O_2N_3Na$ requires 9.46 % sodium.

Thymoquinone and two molecules of semicarbazide hydrochloride.

Attempts were made to prepare a disemicarbazone of thymoquinone by boiling a mixture of an alcoholic solution of thymoquinone with an aqueous solution of two molecules of semicarbazide.The resulting product was not the expected disemicarbazone but 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide.When the mono-condensation product of thymoquinone and semicarbazide hydrochloride was boiled with one molecule of semicarbazide hydrochloride no change took place.

Bromination of 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide.

I. With one equivalent of bromine. Preparation of 2-methyl-5-isopropyl-4-hydroxy-3-monobromobenzeneazoformamide.



2 grams of 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide were dissolved in glacial acetic acid and 6 grams of sodium acetate added and to the solution well cooled with ice water, a solution of 1.6 grams of bromine in glacial acetic acid was slowly added from a dropping funnel. After allowing the mixture to stand for a few hours water was added. A light yellow precipitate was thrown down which was filtered off and washed with water, alcohol and petroleum ether. On crystallising from boiling alcohol yellow needles were obtained which melted with decomposition at 218° and which were soluble in water, alcohol, acetone and glacial acetic acid; slightly soluble in chloroform; insoluble in benzene, carbon disulphide, ether and petroleum ether. The substance is soluble in sodium hydroxide forming a red coloured solution.

0.1637 gm. gave 20.4 c.c. of nitrogen at 21° and 754 mm.

14.07 % nitrogen. $C_{11}H_{14}O_2N_3Br$ requires 14 % nitrogen.

II. With excess of bromine. Preparation of a dibromo-derivative.

8 grams of 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide

were dissolved in glacial acetic acid and 16 grams of sodium acetate added;to the well cooled solution excess of bromine in glacial acetic acid was slowly added from a dropping funnel.After a few hours a little water was added to the reaction mixture;a light yellow precipitate formed which after several crystallisations from boiling alcohol formed yellow needles.The substance melts at 245° and is soluble in water,alcohol,acetone and glacial acetic acid; slightly soluble in chloroform;insoluble in benzene,ether,carbon disulphide and petroleum ether.Sodium hydroxide dissolves the compound forming a dark red solution of the sodium salt.

0.1846 gm. gave 18.4 c.c. of nitrogen at 18° and 744 mm. 11.26 % nitrogen. $C_{11}H_{13}O_2N_3Br_2$ requires 11.08 % nitrogen.

An attempt was made to prepare a hydroxyazo-derivative of dibromothymoquinone (m.p. 74°).

2 grams of dibromothymoquinone obtained from Kahlbaum were dissolved in alcohol and treated with one equivalent of semicarbazide in aqueous solution.After standing overnight yellow needles were obtained which melted at 74°. A melting point of the needles mixed with dibromothymoquinone was taken and found to be 74°.This proves that no reaction had taken place and that the dibromothymoquinone had separated out from solution.

Attempts in glacial acetic acid solution and in alkaline solution with and without the addition of sodium acetate gave simil ar negative results.

The fact that no reaction could be obtained between dibromothymoquinone and semicarbazide hydrochloride makes it doubtful where the second bromine atom attacks 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide,whether it enters the nucleus or the side chain.

Attempt to prepare a semicarbazone of quinonechlorimide.

As the compounds formed by the action of semicarbazide hydrochloride on p-benzoquinone and its derivatives in the proportion necessary for the formation of monosemicarbazones were found to react as hydroxyazo-bodies and also to give absorption spectra characteristic of undoubted azo-bodies,it was considered desirable to attempt to prepare a compound in which the change from a semicarbazone to the isomeric hydroxyazo-body is impossible.(Quinone oximesemicarbazone is such a body but as Thiele and Barlow (Ann. 1898,302,331) state that it is insoluble in water and alcohol,it is unsuitable for the comparison of its spectrum with those of the compounds described in this thesis). With this end in view an attempt was made to prepare a semicarbazone of quinonechlorimide.In such a body there is no possibility of a hydrogen atom wandering from the semicarbazone group to the :NCl group.

P-benzoquinonechlorimide was prepared by reducing p-nitrophenol to p-amidophenol which was then treated with bleaching powder according to the method of Fogh.(Ber.1888,21,890).

4.5 grams of p-benzoquinonechlorimide were dissolved in 50 c.c. of alcohol and after cooling in the ice chest were mixed with an aqueous solution of 3.5 grams of semicarbazide hydrochloride. A yellow precipitate formed immediately but decomposed with evolution of nitrogen before it could be filtered off. This was tried several times and in every case decomposition took place.

Table I.

Compound.	Decomposition point.	Colour.
1. $C_7H_7O_2N_3$	165-166	yellow;red.
2. $C_7H_6O_2N_3Cl$	185	brownish yellow.
3. $C_7H_5O_2N_3Cl_2$	218	yellow:red.
4. $C_7H_5O_2N_3Br_2$	223-225	yellow.
5. $C_8H_{10}O_2N_6$	243	red.
6. $C_9H_{11}O_2N_3$	162	orange red.
7. $C_9H_9O_3N_3$	158	orange red.
8. $C_7H_6O_2N_3Na$		red.
9. $C_7H_6O_2N_3Ag$		red.
10. $C_7H_5O_2N_3ClNa$		red.
11. $C_7H_4O_2N_3Cl_2Na$		red.
12. $C_7H_4O_2N_3Br_2Na$		red.
13. $C_8H_9O_2N_3$	178-179	yellow.
14. $C_8H_8O_2N_3Br$	205	yellow.
15.($C_8H_7O_2N_3Br_2$	225-228	yellow).
16. $C_9H_{12}O_2N_6$	240	orange.
17. $C_8H_8O_2N_3Na$		red.
18. $C_{11}H_{15}O_2N_3$	201-202	yellow.
19. $C_{11}H_{14}O_2N_3Br$	218	yellow.

Table I.(cont.)

Compound.	Decomposition point.	Colour.
20. $C_{11}H_{13}O_2N_3Br_2$	245	yellow.
21. $C_{11}H_{14}O_2N_3Na$		red.

With the exception of numbers 1,4,5 and 6 the compounds are new and are now described for the first time. No.6 has been prepared by a new method.

Action of ultra-violet light upon the hydroxyazoformamides.

4-hydroxybenzeneazoformamide,3-methyl-4-hydroxybenzeneazoformamide and 2-methyl-5-isopropyl-4-hydroxybenzeneazoformamide were dissolved in acetone and exposed in quartz flasks at a distance of 10 centimeters from a quartz mercury vapour lamp for fifteen hours without undergoing any change as was shown by taking the melting points after exposure to the light.In no case was the melting point changed.

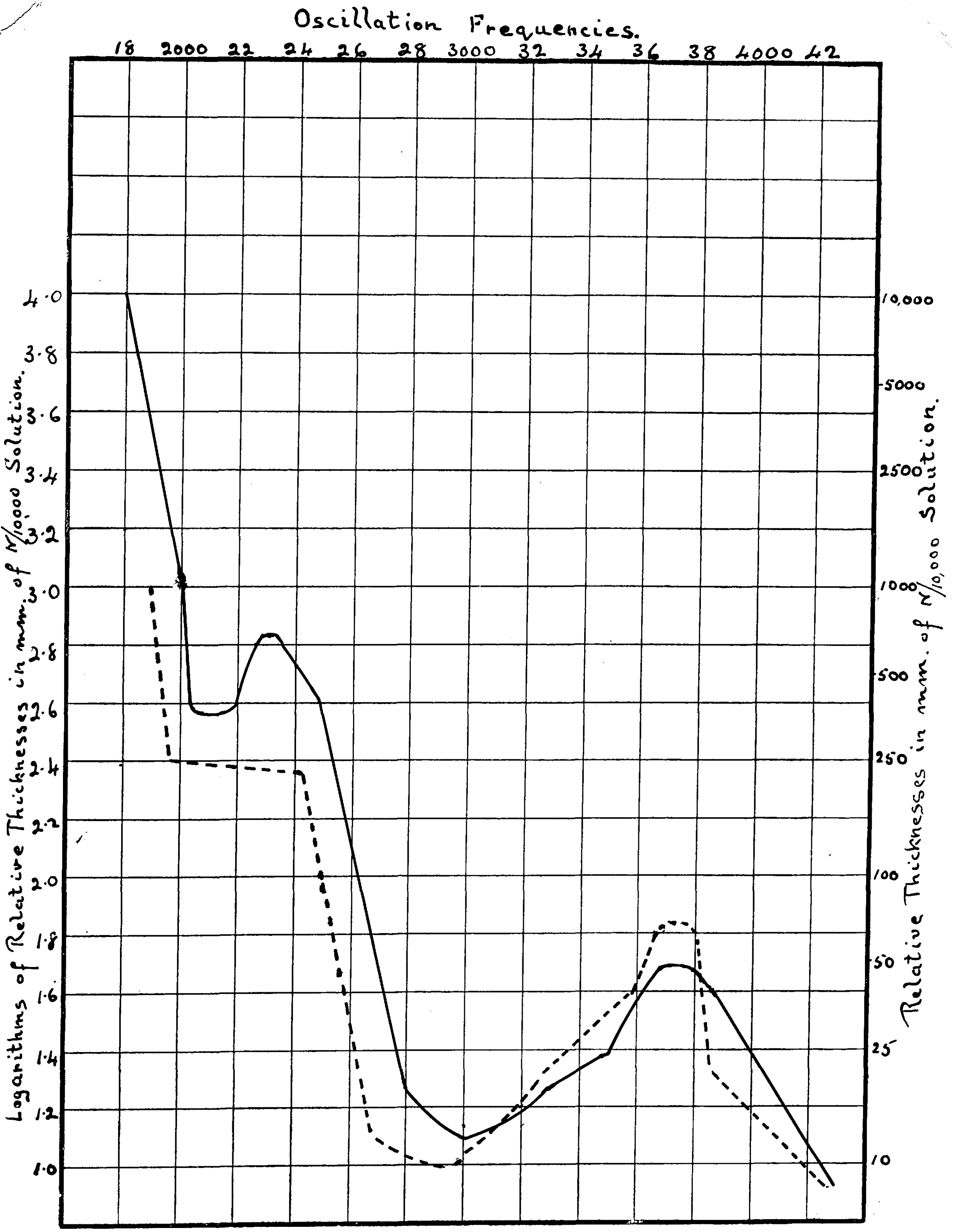
Optical Investigation.

Throughout the optical investigation of the compounds described in the experimental part the absorption spectra were obtained by means of a Hilger's quartz spectrograph which gives a spectrum nearly fifteen centimeters in length extending from $1/\lambda$ 1800 to $1/\lambda$ 4300 oscillation frequencies. The plates used for photographing the spectrum were Wratten and Wainwright's "Allochromatic Plates" and for the absorption in the extreme red the same firm's "Panchromatic Plates". The plates were exposed for fifteen seconds, the source of light being an iron arc, and developed with "Rodinal". The solution to be examined was placed in a Baly's tube and photographs were taken through layers of different thicknesses. The solutions used were generally N/10,000 and N/1000 and in some cases N/100, and photographs were taken through thicknesses of 100, 90, 80, 70, 60, 50, 40, 35, 30, 25, 20, 17, 15, 12, 10, 8, and 6 mm. at each concentration.

The curves shown in the plates were drawn by taking oscillation frequencies as abscissae and the logarithms of the thicknesses in terms of a N/10,000 solution as ordinates according to the method of Baly and Desch.

Plate I. This plate shows the curve obtained for the ethyl ether of 4-hydroxybenzeneazoformamide in alcohol (full line) and that for benzeneazophenetole (dotted line) which has been described by Tuck (Trans. 1907, 91, 451). A glance shows the great similarity of the two curves. Similar curves have been obtained by Hewitt and Thomas (

Plate I.


Oscillation Frequencies.
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10000 Solution.
4·0
3·8
3·6
3·4
3·2
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
Relative Thicknesses in mm. of N/10,000 Solution.
10,000
5000
2500
1000
500
250
100
50
25
10

Trans.1909,95,1295) in the case of aminobenzeneazophenol and by Fox and Pope (Trans.1912,101,1498) in the case of benzeneazophenylmethylmercaptole.These curves are all of the same type as that described by Hartley (Trans.1887,51,152) and by Crymble,Stewart and Wright (Ber.1910,43,1188) for azobenzene.Baly and Tuck (Trans.1906, 89,984) state that the absorption spectrum of azobenzene may be taken as the type of absorption of an azo-body.

The curve for 4-hydroxybenzeneazoformamide has a band at about 2100 of persistence 3 and a deep band at about 3000 of persistence 7.The curve for benzeneazophenetole shows a step-out in place of the band at 2100 and a band at about 2900.The curve for azobenzene described by Crymble,Stewart and Wright (loc.cit.) shows two bands one at 2200 and the other at 3200.

Plate II. This shows the curves for the acetyl derivative of 4-hydroxybenzeneazoformamide in alcohol (full line),in water (dash-dot line) and in chloroform (dotted line).The type of curve is the same as that shown in Plate I.The head of the main band is at about 2980 ; the persistence is 9.The head of the shallow band is at about 2150 with a persistence 1. The three curves do not vary much. The curve is slightly nearer the red in water and chloroform solutions than when the substance is dissolved in alcohol.

Plate II.

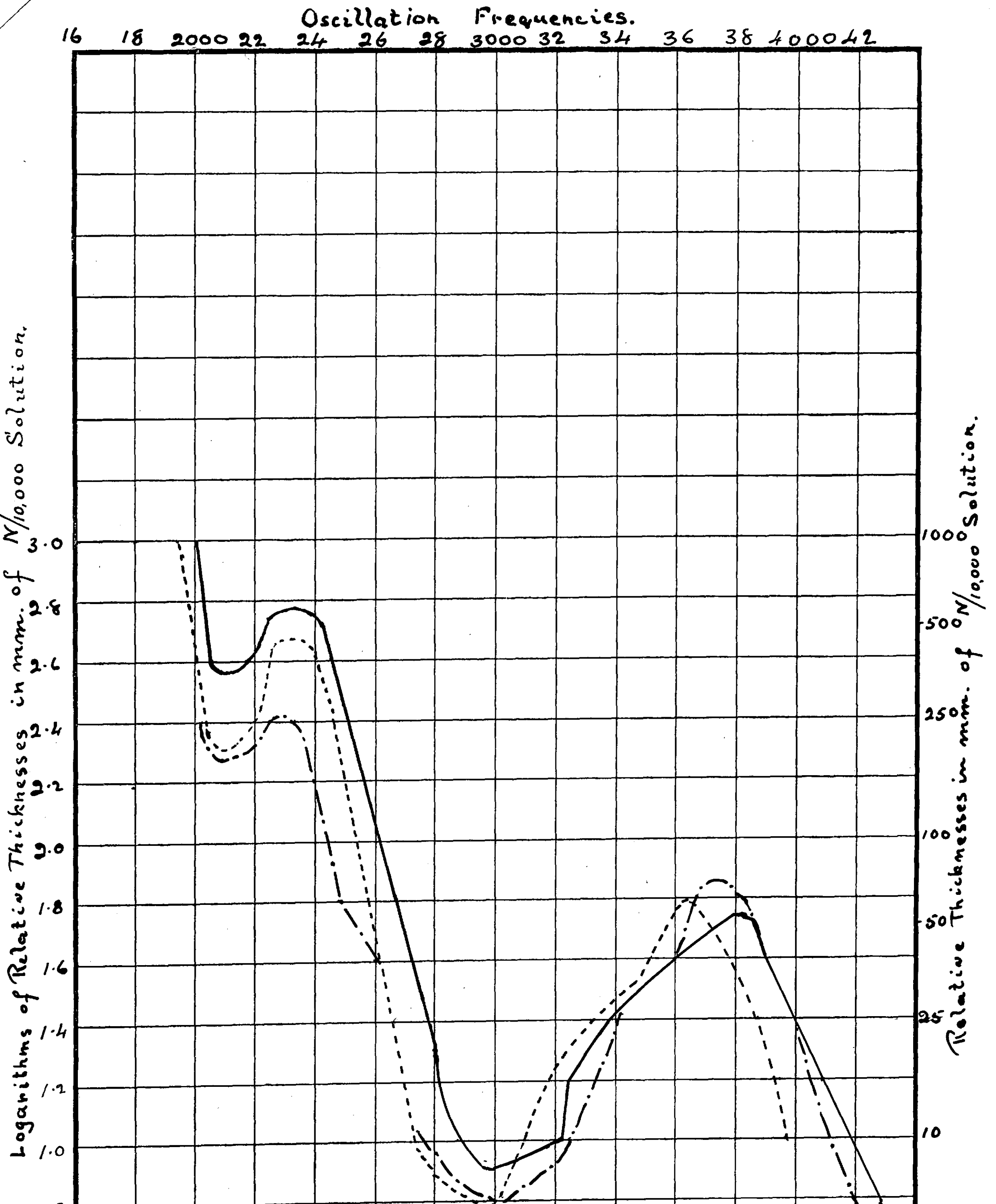

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5

Plate III.

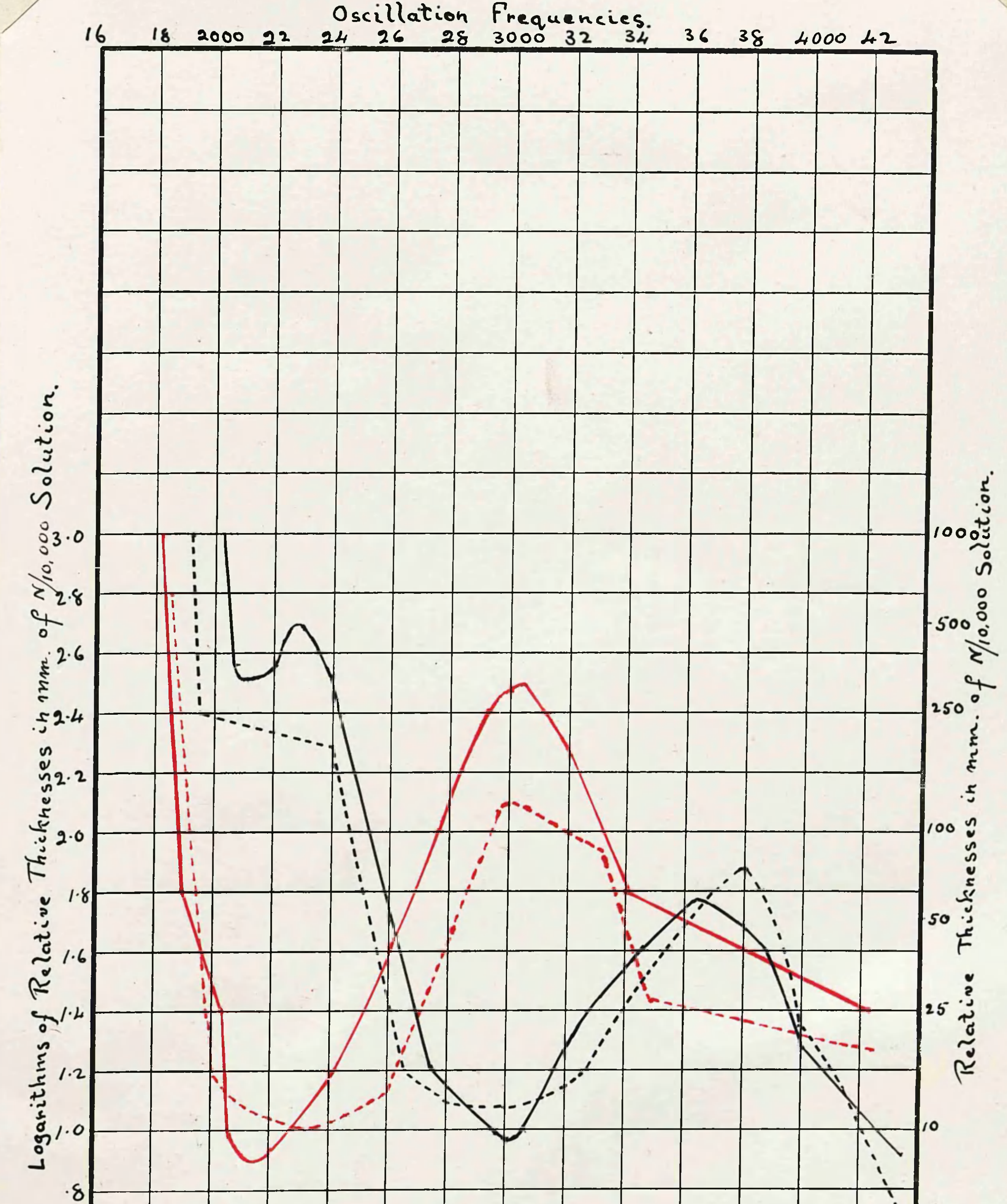

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5

Plate III. In this plate are shown the curves for 4-hydroxybenzeneazoformamide in alcohol (full black line) and for the same substance with excess of sodium ethoxide (full red line);the curves obtained by Tuck (loc.cit.) for benzeneazophenol (dotted black line) and this substance with sodium ethoxide (dotted red line) are reproduced for comparison. Here again the great similarity between the two sets of curves is seen.The effect of sodium ethoxide in each case is to push the band towards the red and practically to the same extent. The curve for 4-hydroxybenzeneazoformamide is of the same type as that shown in Plate I for its ethyl ether;as the latter must be a true azo-body it follows that the former must also be an azo-compound.

The curve for 4-hydroxybenzeneazoformamide has a shallow band at 2100 of persistence 2 and a deep band at 3000 of persistence 8; and the same substance with sodium ethoxide has a deep band at 2100 and a step out from 3200 to 4200.

Plate IV. This plate shows the absorption spectrum of 4-hydroxybenzeneazoformamide in water. The curve is of the same type as that obtained for this substance in alcohol.It shows two bands,one at 2100 of persistence 2.5 and the other at 2800 of persistence 8.

Plate IV.

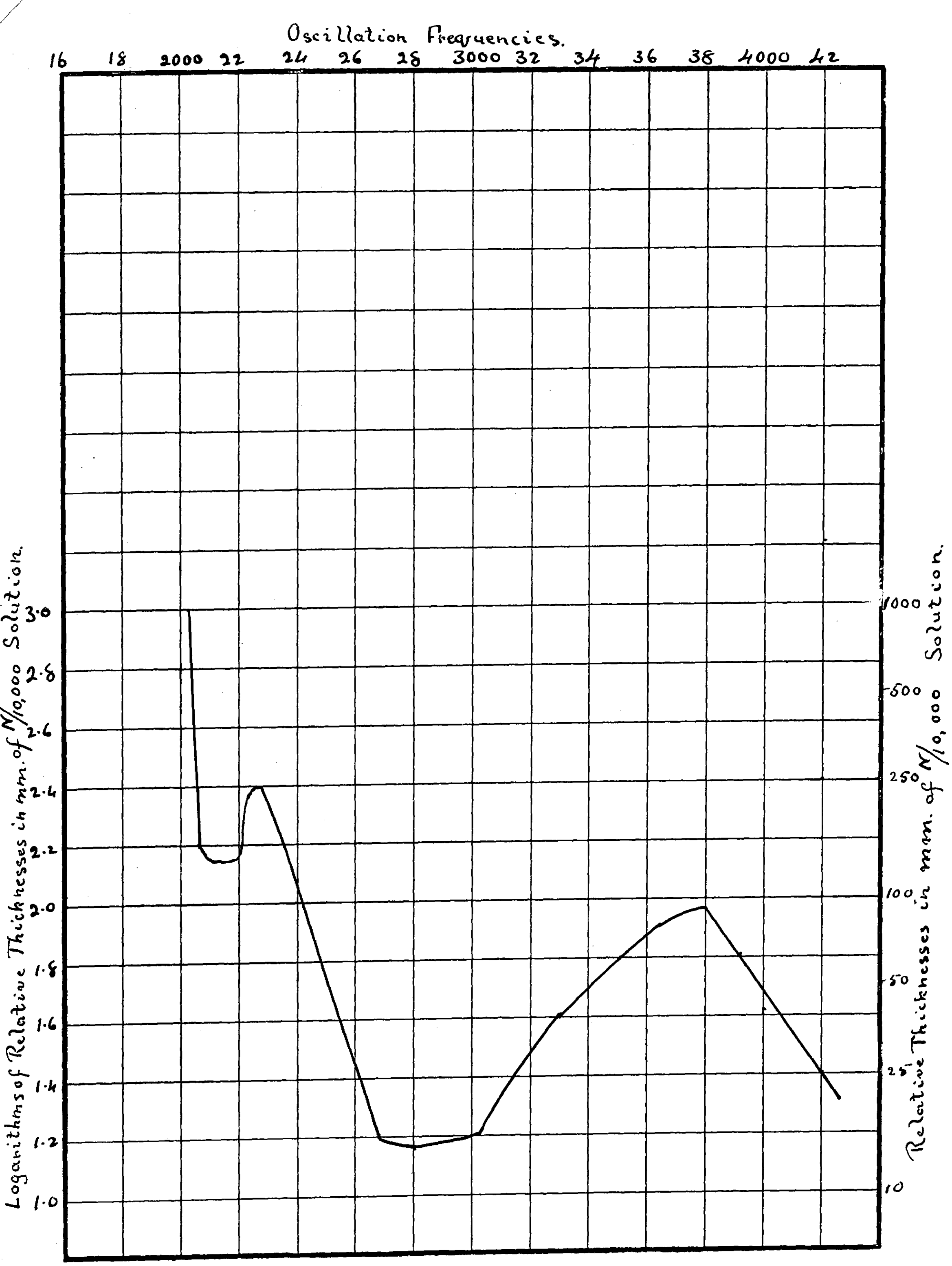

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10

Plate V.

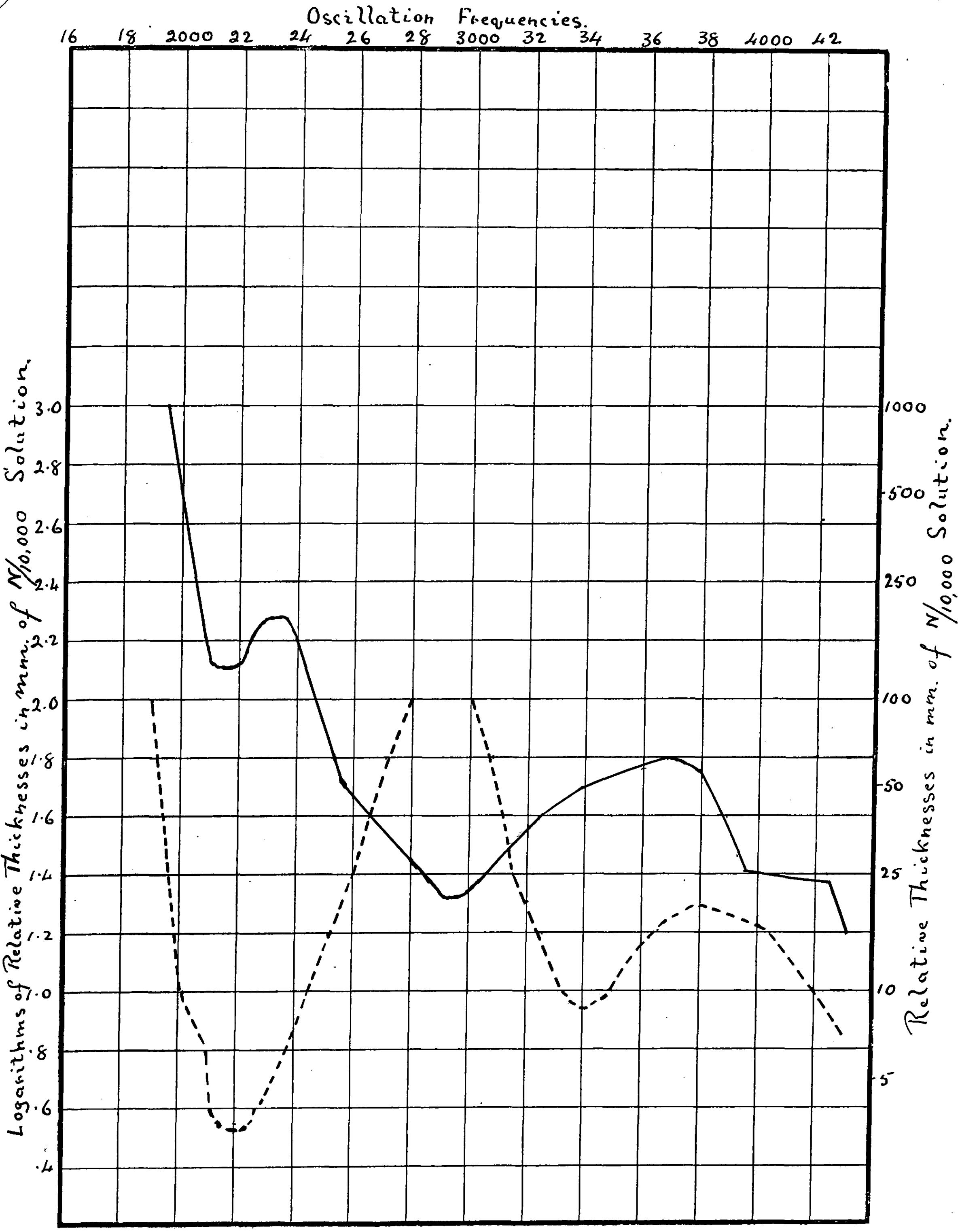

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5

Plate V. The curves for 4-hydroxy-3-monochlorobenzeneazoformamide (full line) and for the same substance with sodium ethoxide (dotted line) are shown in this plate.The same types of curves are obtained as in previous plates. The parent substance shows a band at 2100 of persistence 2 and a deep band at 2950 pf persistence 4. The effect of sodium is to push the band towards the red; the band is then at 2200 and of persistence 15;in addition there is a second band at 3400 of persistence 3.This latter band occupies the place of the step-out in the case of 4-hydroxybenzeneazoformamide with sodium ethoxide.

Plate VI shows the curves for 4-hydroxy-3:5-dichlorobenzeneazoformamide (full line) and the same substance with excess of sodium ethoxide (dotted line). The first shows a band at 2100 of persistence 1.5 and a deep band at 2950 of persistence 7.5. The effect of sodium is seen in the pushing of the band to the red end of the spectrum;the band is at 2100 and of persistence 16.The second band is at 3500 and of persistence 2. A deviation from Beer's law is also to be noted.

Plate VII. The absorption spectra of 3-methyl-4-hydroxybenzeneazoformamide in alcohol (full black line) and in water (full red line) and the same substance with sodium ethylate (dotted line) are drawn

Plate VI.

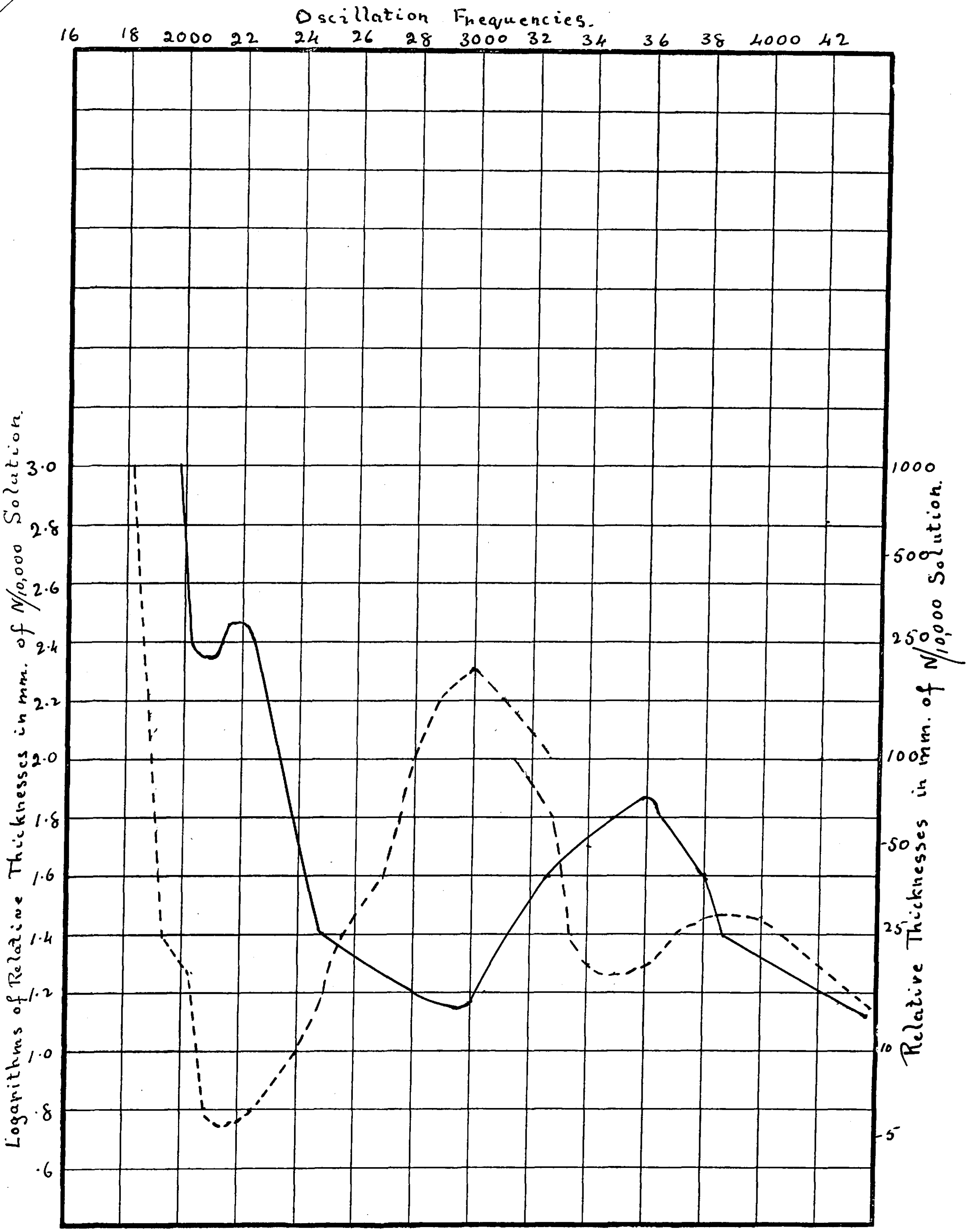
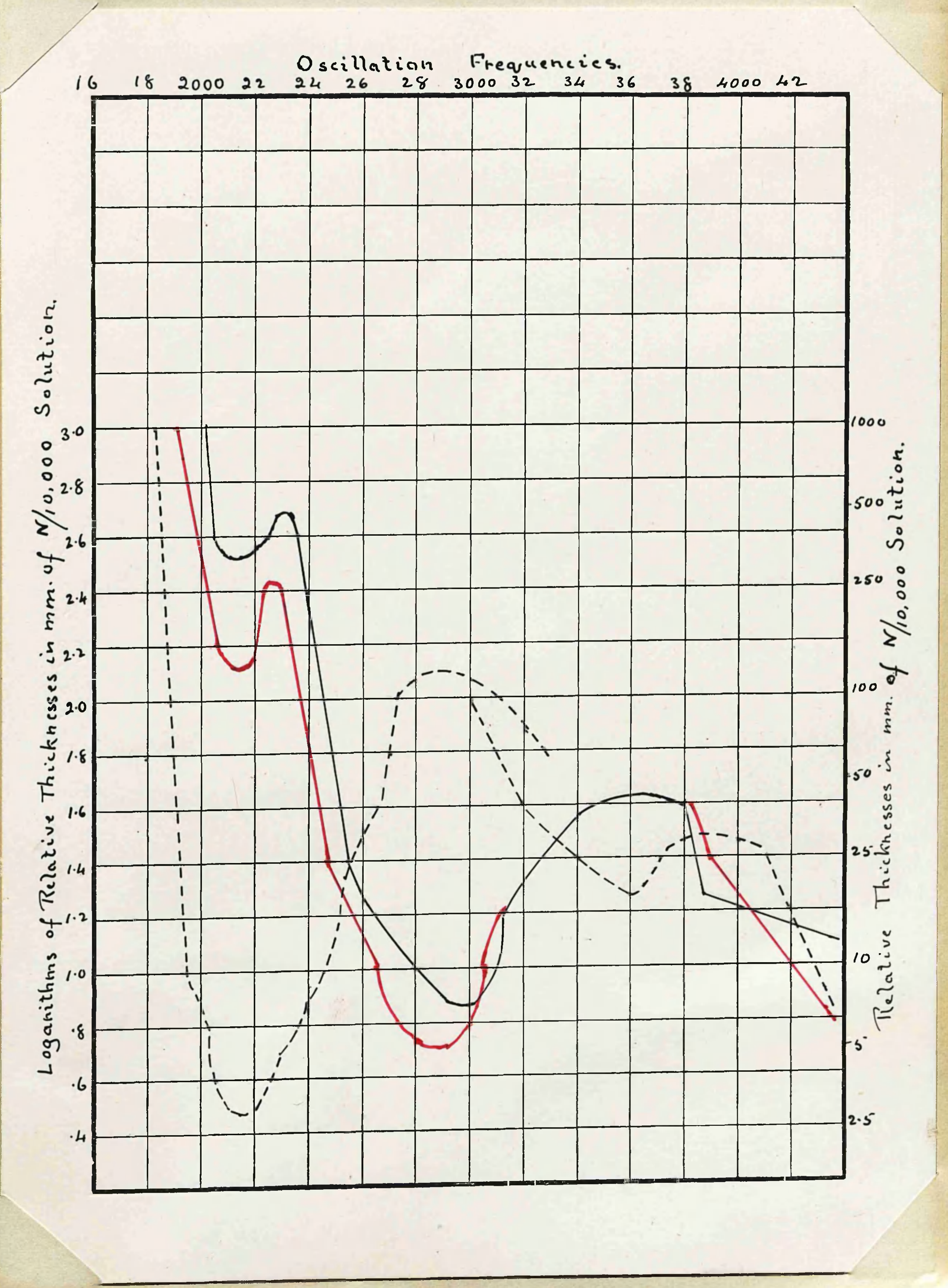

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5

Plate VII.


Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5
2.5

The former shows two bands,one at 2100 of persistence 2 and a second one at 3000 of persistence 8. The latter curve shows the effect of sodium ethoxide;the band is pushed to the red and has its head at 2200 and is of persistence 17; a second band occurs at 3600 of persistence 2.5. There is a deviation from Beer's law in the case of compound with sodium ethoxide.

Plate VIII. The full curve is the absorption spectrum of 3-methyl-4-hydroxy-5-monobromobenzeneazoformamide in alcohol; the dotted curve shows the effect of sodium ethoxide. The former shows two bands one at 2100 of persistence 2 and the other at 2900 of persistence 7. The addition of sodium ethoxide pushes the band to the red;the band has its head at 2100 and is of persistence 15,a second band is at 3450 and of persistence 5.

Plate IX shows absorption spectra of 2-methyl-5-isopropyl-4-hydroxy benzeneazoformamide in alcohol (full line) and of the same substance with excess of sodium ethoxide (dotted line).The former shows two bands one at 2100 of persistence 2 and the other at 2800 of persistence 8.The latter curve also shows two bands one at 2100 of persistence 17 and the other at 3400 of persistence 4. There is a deviation from Beer's law.

Plate VIII.

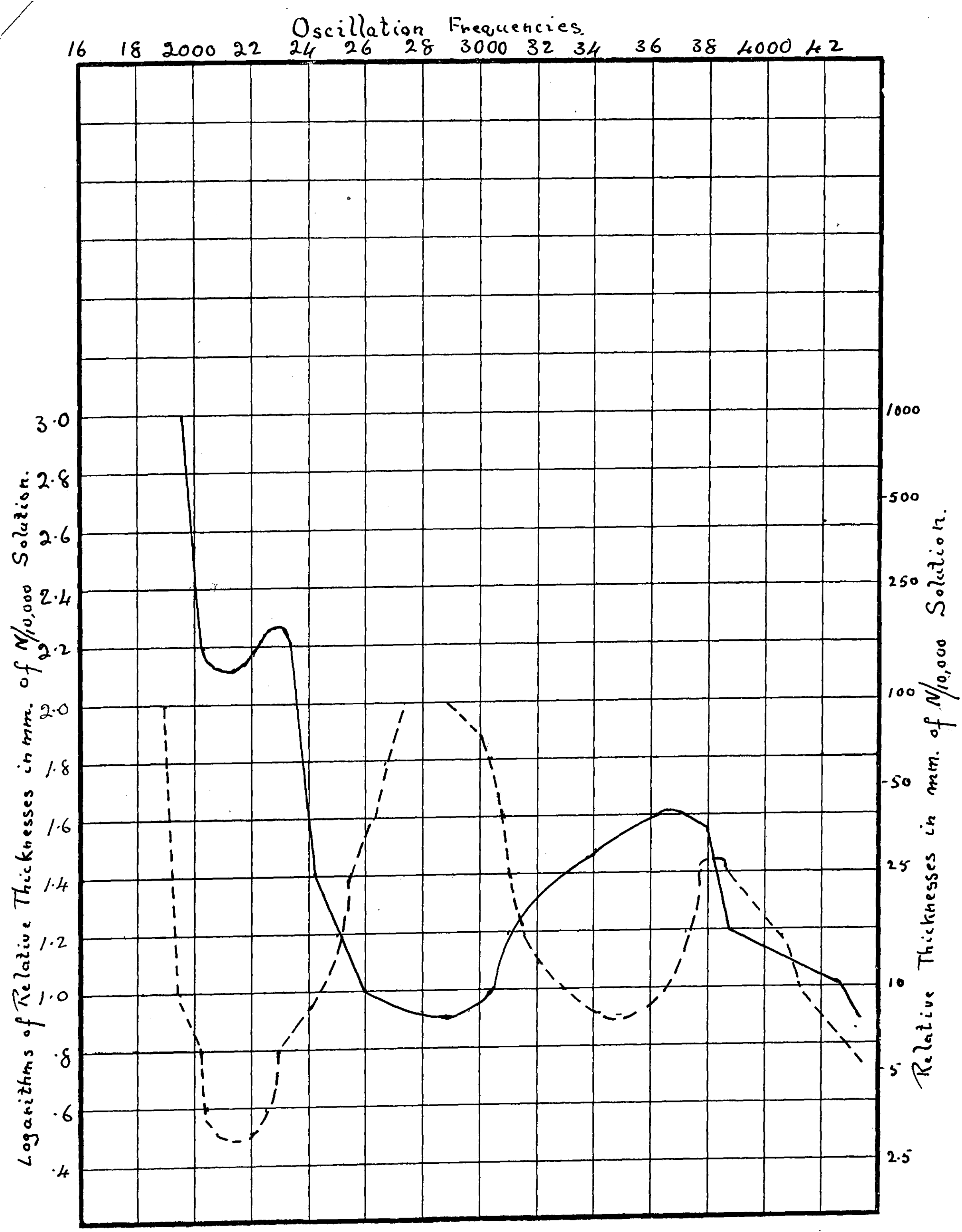

Oscillation Frequencies
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
·8
·6
·4
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5
2·5

Plate IX.

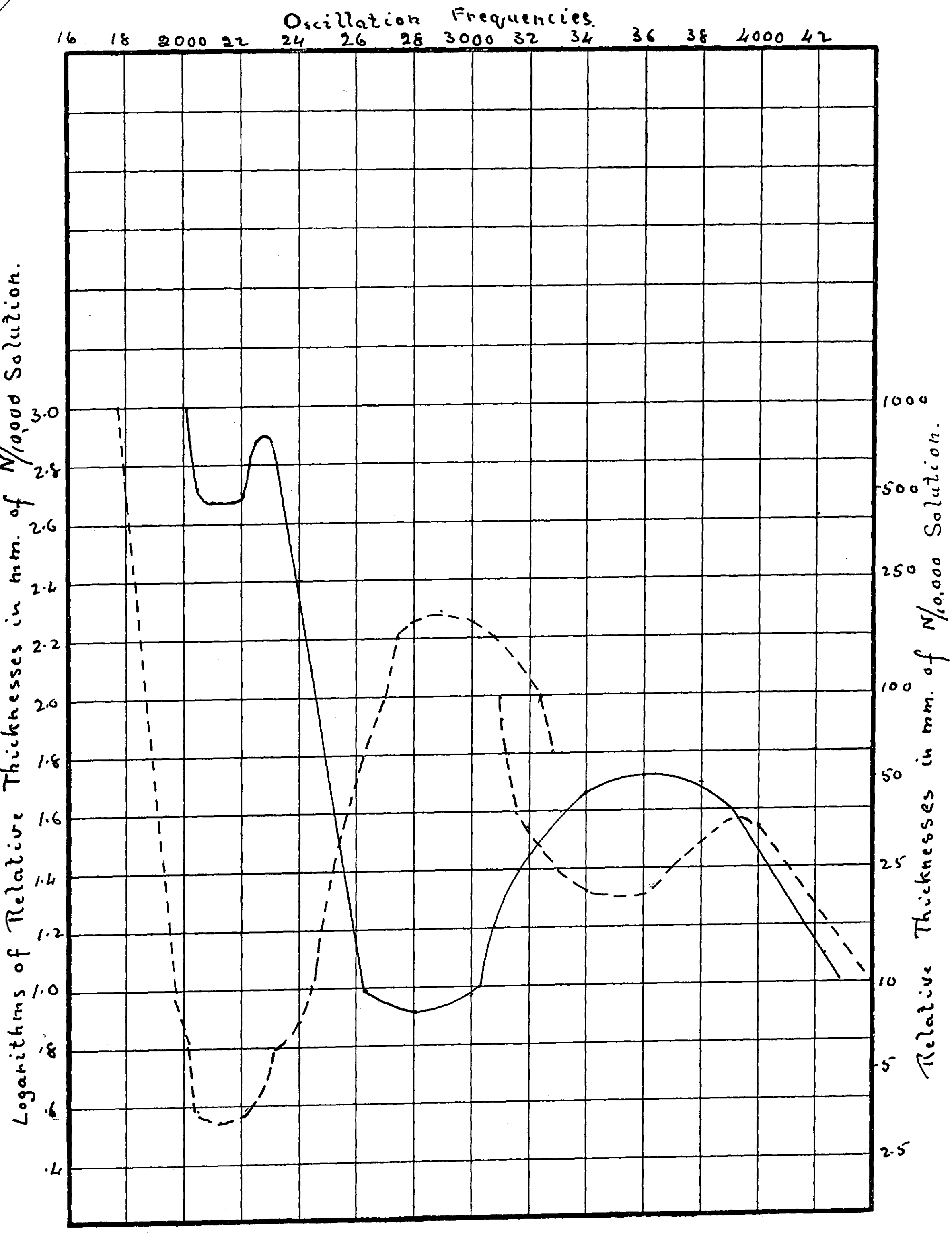

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
1000
500
250
100
50
25
10
5
2.5
Relative Thicknesses in mm. of N/10,000 Solution.

Plate X. This shows the curves obtained from 2-methyl-5-isopropyl-4-hydroxy-3-monobromobenzeneazoformamide in alcohol (full line) and the same substance with excess of sodium ethoxide (dotted line) The former has two bands,one at 2100 or persistence 1 and the other at 2800 of persistence 8.The latter has also two bands , one 2100 of persistence 17 and the other at 3400 of persistence 4.The effect of sodium ethoxide is seen to be the pushing of the band to the red end of the spectrum.There is a deviation from Beer's law.

Plate XI shows the absorption spectra of 2-methyl-5-isopropyl-4-hydroxy-3:?-dibromobenzeneazoformamide in alcohol (full line) and of the same substance with sodium ethoxide (dotted line). The former shows two bands one at 2100 of persistence 1 and the other at 2700 of persistence 8. The effect of sodium ethoxide is to push the band to the red;two bands are seen,one at 2100 of persistence 19 and the other at 3500 of persistence 4. There is a deviation from Beer's law.

Plate X.

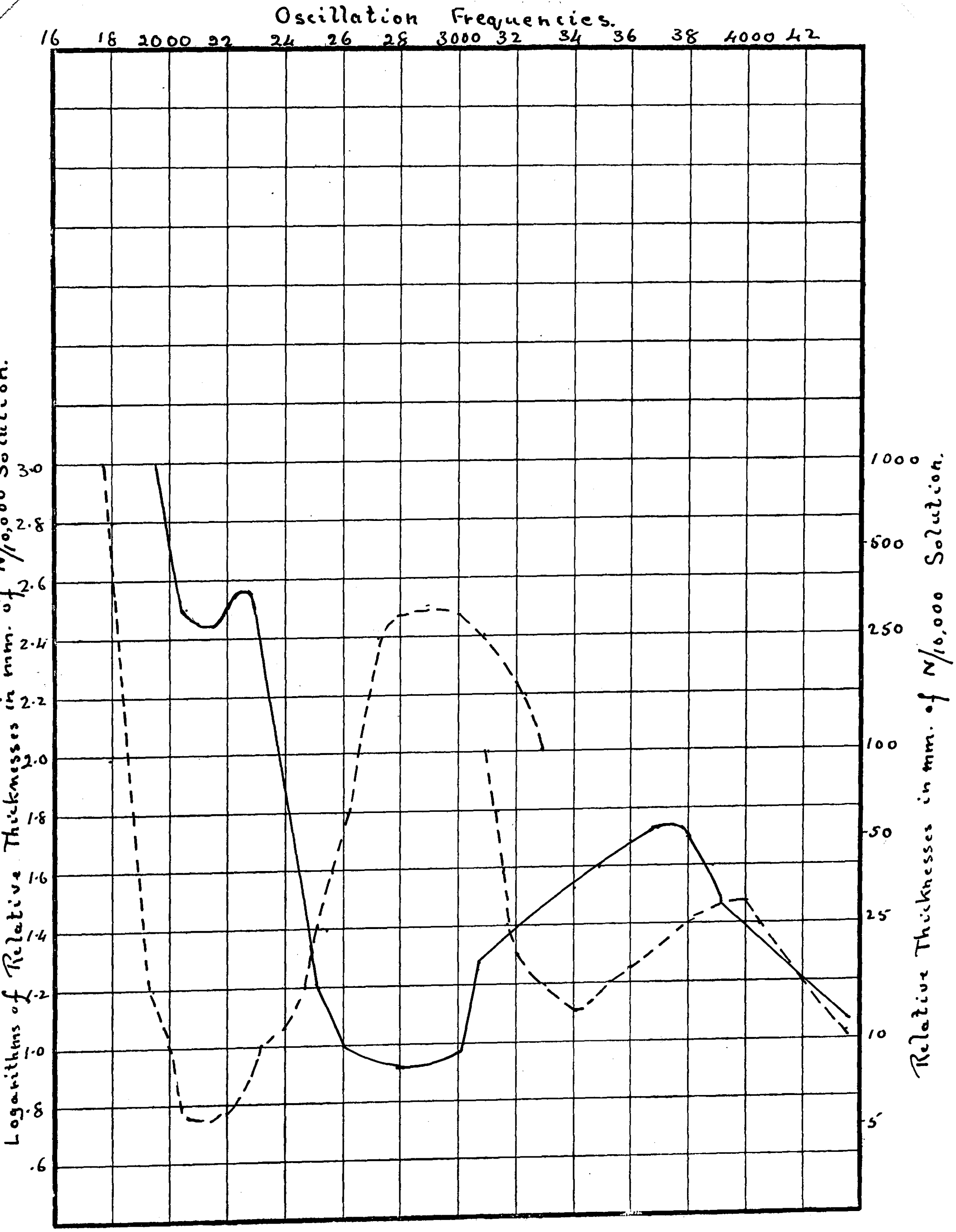

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5

Plate XI.

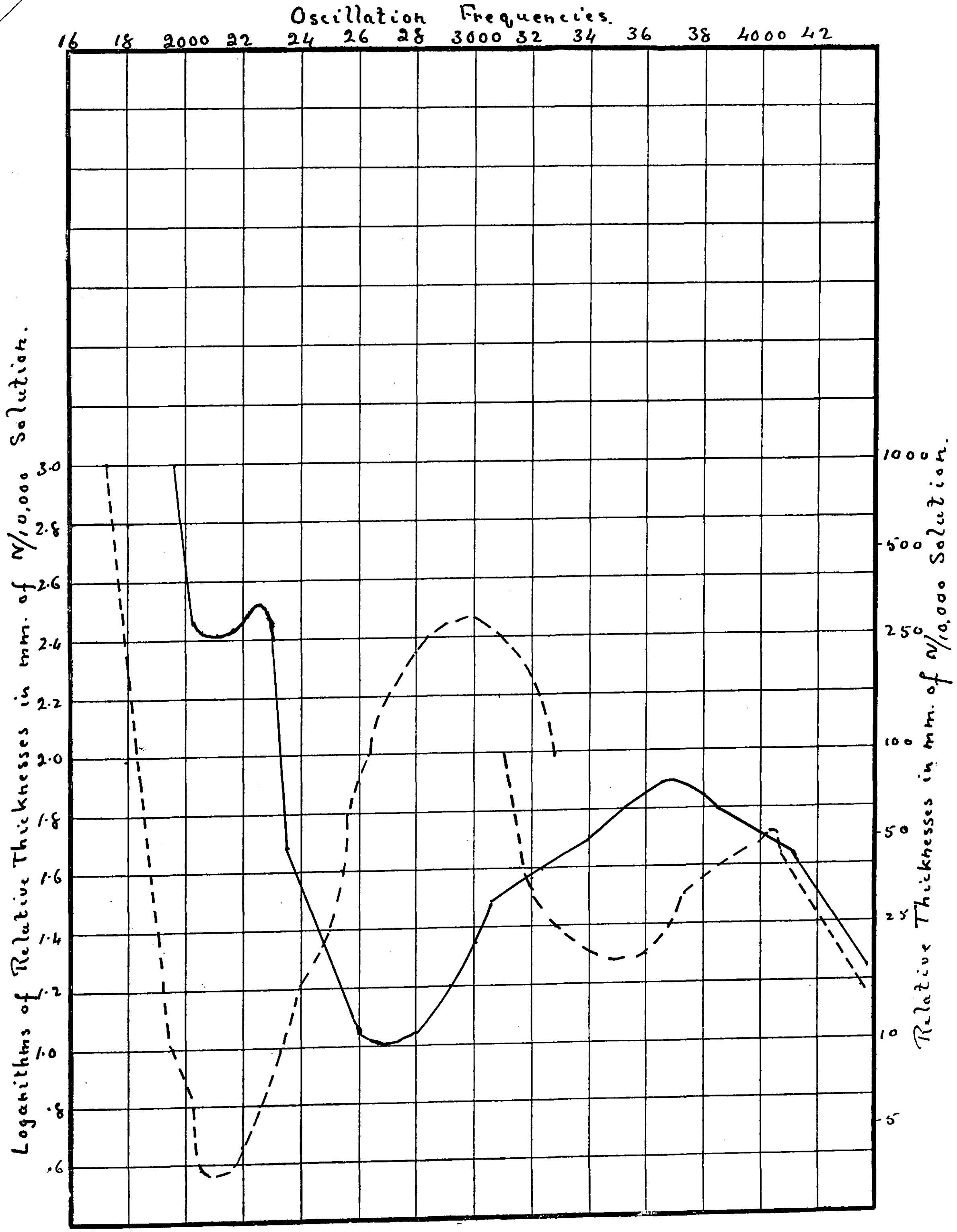

Oscillation Frequencies.
16
18
2000
22
24
26
28
3000
32
34
36
38
4000
42
Logarithms of Relative Thicknesses in mm. of N/10,000 Solution.
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
Relative Thicknesses in mm. of N/10,000 Solution.
1000
500
250
100
50
25
10
5

TABLE II.

Compound.	Molecular weight.	Head of band.	k	Difference from mean value 2174.
$C_7H_7O_2N_3$	165	3000	2165	-9
$C_8H_9O_2N_3$	179	3000	2179	5
$C_9H_{11}O_2N_3$	193	3000	2193	19
$C_7H_6O_2N_3Cl$	199.5	2950	2167	-7
$C_9H_9O_3N_3$	207	2950	2174	0
$C_{11}H_{15}O_2N_3$	221	2900	2154	-20
$C_7H_5O_2N_3Cl_2$	234	2900	2167	- 7
$C_8H_8O_2N_3Br$	258	2900	2191	17
$C_{11}H_{14}O_2N_3Br$	300	2800	2167	- 7
$C_{11}H_{13}O_2N_3Br_2$	379	2700	2179	5
		Mean	2174	

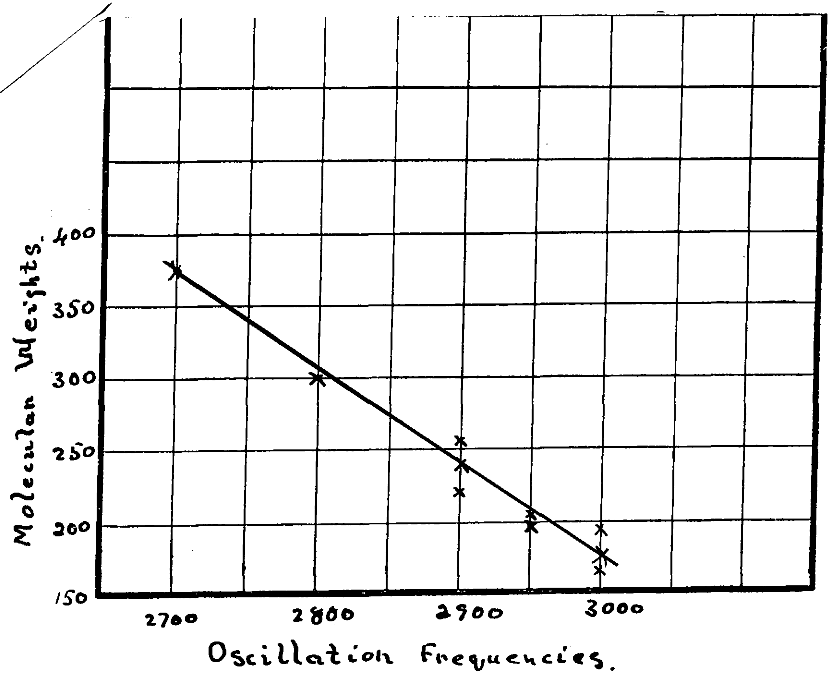
Plates I to XI show curves which are all of the same type, the type being that of azobenzene and benzeneazophenol and their derivatives.

There is a deviation from Beer's law only in the case of the sod-derivatives.

Table II shows the compounds arranged in accordance with their molecular weights; in the third column the heads of the principal band of the compounds are given and it is to be noted that an increase in molecular weight is accompanied in general with a pushing of the band towards the red end of the spectrum.

The points plotted by taking the heads of the band as abscissae and the molecular weights as ordinates are found to lie approximately on a straight line as shown in Plate XII.

Plate XII.



Taking the simplest equation to a straight line

$$y = mx + k \qquad (a)$$

and substituting M (molecular weight) for y and $\frac{1}{\lambda}$ (head of band) for x,this becomes $$M = m\frac{1}{\lambda} + k \qquad (b)$$

On giving numerical values to M and ,the value -2/3 is found for m, thus,

$$179 = m\,3000 + k$$

$$\underline{379 = m\,2700 + k}$$

$$\text{whence } m = -2/3$$

After substituting -2/3 for m in equation (b) and transposing,equation (c) is obtained

$$k = 2/3(\frac{1}{\lambda}) + M \qquad (c)$$

The values for k given in the fourth column of Table II have been calculated from this equation;the figures in the fifth column show the differences between the calculated values for k and the mean value of k (2174).

The values found for k do not vary very greatly and this points to the fact that,in the series of compounds investigated above,there is evidently a close connection between the molecular weight of a compound and the head of its principal band. Such a relationship has not hitherto been observed in any series of compounds examined spectrographically.

Taking the figures given by Tuck (loc.cit.) the following results given in Table III are obtained for the para-compound he examined.

Table III.

Compound.	Molecular weight.	Head of band.	k	Difference from mean value 2174.
$C_{12}H_{10}ON_2$	198	about 3000	2198	24
$C_{13}H_{12}ON_2$	212	" 2900	2145	-29
$C_{14}H_{14}ON_2$	226	" 2900	2159	-15
$C_{15}H_{16}ON_2$	240	" 2900	2173	- 1

Here again the differences between the values for k and the mean value 2174 (Table II) are not very large.

Further investigation is in progress with regard to the relationsh which exists between the molecular weight of a compound (in a series of compounds) and the head of its band.

The investigation which is the subject of this thesis was carried out in the Organic Chemistry Laboratory at the Royal Technical College, Glasgow, and the author takes this opportunity of thanking Professor G. G. Henderson for permission to work in his Laboratory and also for his interest in the work during its progress.