100. *A Potentiometric Study of the Oxidation of Phenylhydrazine by Cupric Ions, including the Titration of Fehling's Solution with Phenylhydrazine.*

By H. T. S. Britton and E. May Clissold.

The oxidation of phenylhydrazine by cupric ions present in complex solutions, *viz.*, as tartrate, together with caustic alkali, borax, or alkali phosphate, acetate, or carbonate, has been investigated potentiometrically at 93°. Benzene and phenol are formed simultaneously, and the results show that, when the difference between the potentials set up at a platinum electrode before and after the completion of the oxidation is small, the amount of benzene formed predominates, but when the difference is large a greater proportion of phenol is produced. Under carefully controlled conditions in regard to the reactants, the potentiometric method is particularly suitable for the quantitative estimation of phenylhydrazine with an accuracy greater than that of the usual gasometric nitrogen method.

Britton and Königstein (J., 1940, 673) have shown that hydrazine and hydroxylamine may be potentiometrically estimated by means of Fehling's solution at 90°. The present work is an extension of this method to the estimation of phenylhydrazine. Unlike that of hydrazine and hydroxylamine, however, the oxidation of phenylhydrazine cannot be expressed by a definite stoicheiometric equation, and this militates against the titration as a quantitative method, but if precautions are taken with regard to (*a*) temperature and (*b*) concentrations of the reactants, the method is capable of yielding results that are more accurate than those obtained by the usual method in which the volume of nitrogen evolved is measured (Strache, see Smith, *Chem. News*, 1906, **93**, 83; Thorpe and Whiteley, "Organic Chemical Analysis," London, 1925, p. 182; Ellis, J., 1927, 848; Marks and Morrell, *Analyst*, 1931, **56**, 512).

Phenylhydrazine on oxidation with Fehling's solution yields benzene and phenol in approximately equimolecular ratio. At room temperature the reaction is slow, requiring ½ hour for completion (Maclean, *Biochem J.*, 1913, **7**, 511; Marks and Morrell, *loc. cit.*), whereas at 93° the present work shows that it is almost instantaneous. The equation usually assigned to the reaction is

$$2C_6H_5\cdot NH\cdot NH_2 + 6CuO \longrightarrow C_6H_6 + C_6H_5\cdot OH + 2N_2 + 2H_2O + 3Cu_2O$$

but calculation from Maclean's data shows that benzene and phenol were produced at room temperature in the ratio of 17 : 83, whereas Marks and Morrell's data reveal variations in this ratio between 37·5 : 63·5 and 48·5 : 51·5. It is clear, therefore, that the oxidation process consists of two separate reactions, *viz.*,

$$C_6H_5\cdot NH\cdot NH_2 + 2CuO \longrightarrow C_6H_6 + N_2 + H_2O + Cu_2O$$

and

$$C_6H_5\cdot NH\cdot NH_2 + 4CuO \longrightarrow C_6H_5\cdot OH + N_2 + H_2O + 2Cu_2O$$

and as the phenylhydrazine evolves all its nitrogen in each reaction this fact does not invalidate Ellis's method. It does, however, interfere with any method, either gravimetric or volumetric, based on the amount of cuprous oxide precipitated. The following titrations show that at 93° the ratio of the two processes is materially influenced by the concentrations of the reactants employed.

It was thought probable that the particular process taking place would be largely determined by the oxidation potential, E, established in the complex cupric solution. For $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \boldsymbol{F}$

$$E_{Cu^{\cdot\cdot} \rightarrow Cu^{\cdot}} = \varepsilon_{Cu^{\cdot\cdot} \rightarrow Cu^{\cdot}} - (\boldsymbol{RT}/\boldsymbol{F}) \log_e [Cu^{\cdot}]/[Cu^{\cdot\cdot}]$$

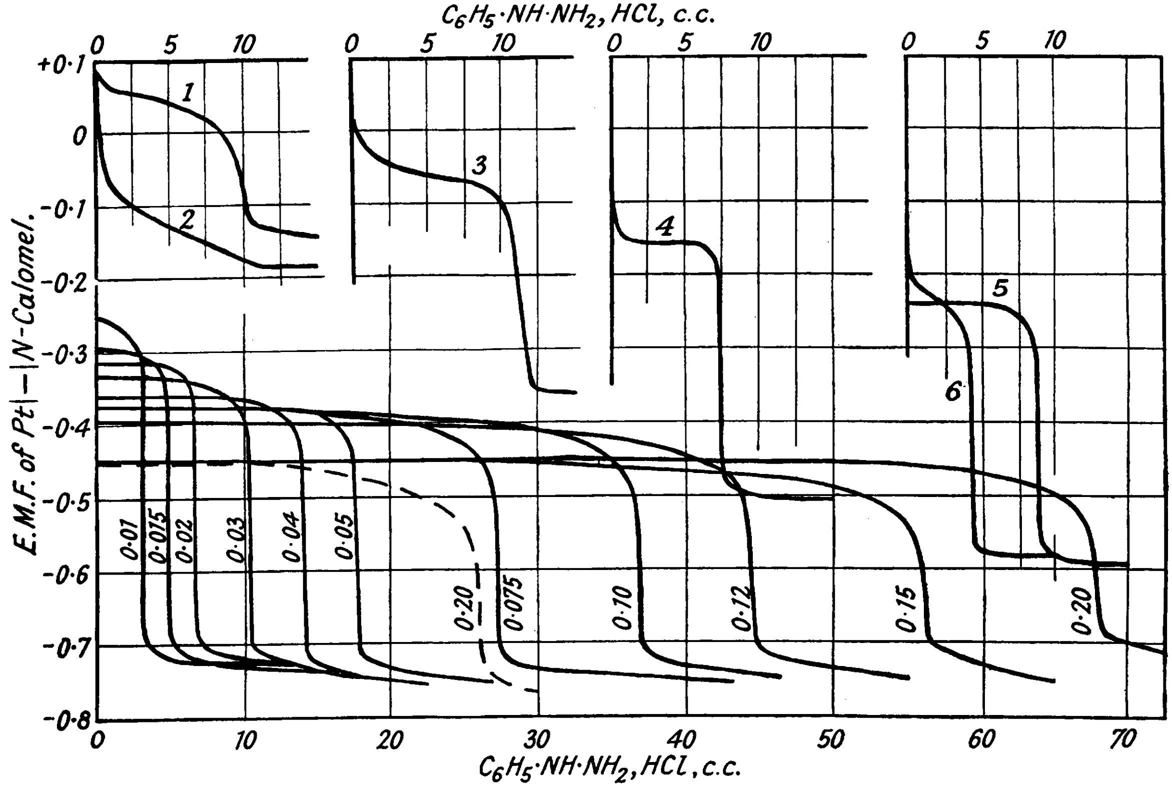
hence the actual oxidation potential, $E_{Cu^{\cdot\cdot} \rightarrow Cu^{\cdot}}$, will depend on the ratio $[Cu^{\cdot}]/[Cu^{\cdot\cdot}]$, and, as cuprous oxide is always precipitated, the $[Cu^{\cdot}]$ will be determined by $[OH']$, and consequently by the p_H. Similarly, the $[Cu^{\cdot\cdot}]$ will be governed by the concentration of the solution and the constitution of the complex cupric salt. For this reason the p_H of the complex alkaline cupric tartrate solution was varied by the introduction of alkaline buffers, *viz.*, borax and disodium hydrogen phosphate, and also the behaviour of other complex cupric solutions, which may be buffered in the acid and the neutral range, was investigated.

EXPERIMENTAL.

The titration cell used was

Pt	100 c.c. of Cu solution x c.c. of $C_6H_5{\cdot}NH{\cdot}NH_2,HCl$	Satd. KCl	N-KCl	N-KCl Hg_2Cl_2	Hg

It was immersed in a water-bath, the temperature of which was regulated at 93° ± 1°. To prevent atmospheric oxidation, the titration cell was closed with a tightly fitting ebonite cap. Nitrogen was used to maintain an oxygen-free atmosphere above the solution and also to agitate the solution after each addition of titrant. To ensure that reproducible potentials were being indicated, two bright platinum electrodes were used and the *P.D.*'s between each electrode and the normal calomel electrode were measured.



Effect of Concentration of Fehling's Solution and Phenylhydrazine Hydrochloride Solution.—Some titrations were performed of phenylhydrazine hydrochloride with Fehling's solution as the titrant, but the potentials set up were not always steady, nor were the titration curves completely reproducible. Two difficulties were encountered : (i) the p_H varies over a wide range in the course of the titration, and (ii) the unattacked phenylhydrazine is appreciably volatile at 93°. The volatility was particularly evident in a series of titrations of phenylhydrazine in the presence of an excess of alkali added to stabilise the p_H. In consequence, the above procedure was reversed, the cupric solutions being tartrate with phenylhydrazine hydrochloride. The presence of the combined hydrochloric acid in the latter did not introduce any great variations in the p_H of the solution undergoing titration as there was always present an excess of alkali or buffering agent.

The complex alkaline cupric tartrate solutions were prepared from copper sulphate, sodium tartrate, and sodium hydroxide in the molecular ratio 1 : 4·6 : 10 as used in Fehling's solution. Sodium tartrate was substituted for Rochelle salt as previous work has shown that this change does not affect the oxidation. Table I gives details of the titrations of 100 c.c. of Fehling's solution, the initial concentrations of copper sulphate ranging from 0·01M to 0·2M. The phenylhydrazine hydrochloride was 0·1M, except in the cases of the 0·04M- and 0·2M-copper solutions, where it was 0·25M. These titrations are marked with an asterisk. For the titration marked †, twice the relative amount of alkali was present in the complex tartrate solution.

TABLE I.

$CuSO_4$, mols./l.	Titre, c.c.	$\frac{CuSO_4}{NH_2\cdot NHPh}$.	$NH_2\cdot NHPh$, %, converted into C_6H_6.	$C_6H_5\cdot OH$.	$CuSO_4$, mols./l.	Titre, c.c.	$\frac{CuSO_4}{NH_2\cdot NHPh}$.	$NH_2\cdot NHPh$, %, converted into C_6H_6.	$C_6H_5\cdot OH$.
0·010	3·29	3·03	48·5	51·5	0·050	17·66	2·83	58·5	41·5
†0·010	3·35	2·98	51	49	0·075	27·15	2·72	64	36
0·015	5·00	3·00	50	50	0·100	36·7	2·70	65	35
0·020	6·70	2·98	51	49	0·120	44·3	2·71	64·5	35·5
0·030	10·40	2·88	56	44	0·150	56·0	2·68	66	34
*0·040	14·05	2·85	57·5	42·5	0·200	67·8	2·95	52·5	47·5
0·040	5·55	2·87	56·5	43·5	*0·200	25·9	3·24	38	62

The titration curves are plotted in the lower part of the figure, the concentration of the copper sulphate being indicated on each curve. The curve represented as a broken line is a duplicate of the 0·2M-copper curve except that 0·25M-phenylhydrazine hydrochloride was used instead of 0·1M.

The curves show that, as the concentrations of the Fehling's solution are increased, the initial potentials become increasingly more negative, with respect to that of the normal calomel electrode, whereas the final potentials tend to acquire fairly constant values. This fact reduces the drop in potential which occurs at the inflexions when the cupric salt has been reduced entirely to cuprous oxide and the solutions have just become colourless. The curves show clearly that the optimum conditions for potentiometric titration occur when the copper sulphate concentration is very low, preferably 0·01—0·02M. Table I reveals that it is only with these concentrations that the phenylhydrazine is oxidised equally to benzene and phenol. (The data in cols. 4 and 5 were computed from those in col. 3 on the basis of the equations of the two simultaneous oxidations.) With copper sulphate concentrations from 0·03M to 0·15M, col. 3 shows that progressively less cupric salt is required to effect oxidation, with the result that the benzene produced increases to 66%.

Influence of p_H *on the Oxidising Action of Alkaline Cupric Tartrate Solutions.*—In order to ascertain whether p_H had any effect on the oxidising reactions occurring when 0·1M-phenylhydrazine hydrochloride is progressively added to copper sulphate solutions containing sodium tartrate in the ratio of 1 : 4·6 (see above), two series of titrations were carried out in which the complex tartrate solutions were buffered by the substitution for alkali of either borax or a mixture of disodium hydrogen phosphate and sodium hydroxide. Details of these titrations are given in Table II and typical titration curves are shown in the figure, curve No. 4 being that of solutions given in l. 3 of Table II and No. 5 that of solutions given in l. 6. Table II shows that a considerably larger proportion of phenol is obtained, *viz.*, 72·5—74·5% and 68·5—72·5% respectively. The titration curves reveal that, although well-defined inflexions were produced, the actual potentials set up were less negative than those established when alkali only was present.

TABLE II.

Concns. (mols./l.) of $CuSO_4$.	Na_2T.	$Na_2B_4O_7$.		Titre, c.c.	$\frac{CuSO_4}{NH_2\cdot NHPh}$.	$NH_2\cdot NHPh$, %, converted into C_6H_6.	$C_6H_5\cdot OH$.
0·010	0·046	0·10		2·9	3·45	27·5	72·5
0·015	0·069	0·15		4·3	3·48	26	74
0·025	0·115	0·25		7·15	3·49	25·5	74·5
$CuSO_4$.	Na_2T.	Na_2HPO_4.	NaOH.				
0·01	0·046	0·15	0·056	2·96	3·37	31·5	68·5
0·02	0·092	0·30	0·102	5·95	3·36	32	68
0·03	0·138	0·45	0·168	8·7	3·44	28	72

Influence of Complex Formation of Cupric Ions with (a) *Acetate Ion,* (b) *Carbonate Ion, on the Oxidising Action of Bivalent Copper.*—Some type of complex formation takes place between copper sulphate and sodium acetate or sodium carbonate, so much so that excess of either of these salts may be added to copper sulphate solution without causing precipitation despite the fact that the p_H at which basic copper salts are precipitated (p_H 5·4 at 18°) may be very much exceeded. At high temperatures (*e.g.*, 93°) some precipitation does occur from solutions to which sodium carbonate alone has been added; this, however, can be avoided by introduction of some bicarbonate with the carbonate.

TABLE III.

Concns. (mols./l.) of $CuSO_4$.	$CH_3\cdot CO_2H$.	$CH_3\cdot CO_2Na$.	Titre, c.c.	$\frac{CuSO_4}{NH_2\cdot NHPh}$.	$NH_2\cdot NHPh$, %, converted into C_6H_6.	$C_6H_5\cdot OH$.
0·02	0·2	0·2	10·0	2·00	100	—
0·025	5·0	5·0	11·0	2·27	86·5	13·5
0·025	0	5·0	11·0	2·27	86·5	13·5
$CuSO_4$.	$NaHCO_3$.	Na_2CO_3.				
0·01	0·675	0·675	4·3	2·32	84	16

The four titrations of 100 c.c. of solutions indicated in Table III were carried out at 93° with 0·1M-phenylhydrazine hydrochloride and their respective curves are Nos. 1, 2, 3, and 6.

The first titration in Table III is interesting in that it is the only one in which the phenylhydrazine is quantitatively oxidised to benzene. The titration curve (No. 1), however, shows that the completion of the reaction is not represented by a well-defined inflexion, but merely by an unsatisfactory "break." Curve No. 2 shows a small inflexion.

Discussion.—The curves show that the potentials of the platinum electrode, with respect to that of the normal calomel, set up during the initial and the final stages of the various titrations were largely influenced by the p_H values of the complex cupric salts being titrated. With the most alkaline tartrate solutions (Table I), an increase in the copper sulphate concentration from 0·01M to 0·15M causes an increase in the relative proportion of the benzene to the phenol produced. Lowering the p_H of the complex tartrate solution by means of either borax or sodium phosphate (Table II) reduces the amount of benzene as compared with phenol, whereas the reverse is true in the case of the low p_H complex acetate solutions and alkaline complex carbonate solutions. It was thought that these wide variations in the relative amounts of benzene and phenol might be accounted for by differences in the redox potentials corresponding to the complex copper solutions when compared with the potentials which would be acquired by the hydrogen electrode, assuming it to function reversibly, in the respective solutions. Such variations could only be established by large changes in the value of the ratio $[\mathrm{Cu}^{\cdot}]/[\mathrm{Cu}^{\cdot\cdot}]$. Calculation shows that, although differences do occur, they appear to be too small to explain the variations in the relative amounts of benzene and phenol formed in the course of these titrations. It was considered that a large redox potential would cause oxidation to proceed chiefly to phenol, whereas a small potential would cause it to proceed only as far as benzene.

Perhaps a more satisfactory way of considering this problem is to compare the initial titration potentials with those set up after the end-point has been passed. Curves Nos. 1 and 2 (complex acetate solutions) certainly reveal small differences between initial and final potentials; to a less extent, this is also shown by curve No. 3, and it is interesting that in these titrations the largest yields of benzene were produced. The batch of curves shown in the lower part of the figure, show that, whilst the final potentials assume tolerably constant values, the initial potentials become lower with increasing copper sulphate concentration, and it is very probable that it was these smaller differences which led to the increasingly greater proportions of phenylhydrazine being oxidised to benzene.

Britton and Königstein (J., 1940, 673) advanced evidence to support the view that potentiometric titrations of complex bivalent copper solutions, unlike other " redox " titrations, were made possible by the two successive reactions (i) $\mathrm{Cu}^{\cdot\cdot} \longrightarrow \mathrm{Cu}^{\cdot} + \boldsymbol{F}$ and (ii) $\mathrm{Cu}^{\cdot} \longrightarrow \mathrm{Cu} + \boldsymbol{F}$, equilibria involving (i) and (ii) being responsible respectively for the potentials in the initial and the final section of the graph. It is well known that copper may be deposited in the form of a mirror or else in a finely divided state from complex copper tartrate solution to which an excess of phenylhydrazine has been added. Although large excesses of phenylhydrazine were never added in these titrations, copper deposits were occasionally clearly visible on the electrodes.

Further evidence in support of this view is forthcoming from the final potentials observed in the titrations. They have the added advantage that they refer to solutions having p_H values extending over a wide range. It follows from the method of calculation adopted by Britton and Königstein (*loc. cit.*, p. 675) that the potential set up at a platinum electrode, E_{Pt} at 93°, corresponding to the equilibrium $\mathrm{Cu}^{\cdot} \rightleftharpoons \mathrm{Cu}$ is

$$\begin{aligned} E_{\mathrm{Pt}} &= \varepsilon_{\mathrm{Cu}^{\cdot} \rightarrow \mathrm{Cu}} - 0{\cdot}073 \log L_{\mathrm{CuOH}}/[\mathrm{OH}'] \\ &= \varepsilon_{\mathrm{Cu}^{\cdot} \rightarrow \mathrm{Cu}} - 0{\cdot}073 \log L_{\mathrm{CuOH}} - 0{\cdot}073 \log K_w - 0{\cdot}073\, p_H \end{aligned}$$

Assuming that $\varepsilon_{\mathrm{Cu}^{\cdot} \rightarrow \mathrm{Cu}}$ (0·52 volt at 18°, N-H = 0) and L_{CuOH} (approx. 10^{-14} at 18°) are not materially altered by increasing the temperature to 93°, and taking K_w to be equal to $10^{-12\cdot5}$ at 93°, we can calculate E_{Pt} for any p_H value, and consequently the potential of the platinum electrode against the normal calomel electrode can be computed, for Britton and Welford (J., 1937, 1846) have found that the potential of the latter (N-H = 0) at 91° is + 0·263 volt. Thus, in the complex tartrate titrations, the $[\mathrm{OH}']$ varied from about 10^{-1} to almost 1M, and therefore the p_H ranged from 11·5 to 12·5. The potentials assumed by the platinum electrode should therefore fall within the range − 0·69 to − 0·76. The potentials corresponding to the final sections of the series of curves at the bottom of the figure show that this is the case.

The p_H in the complex tartrate–borax titration was approximately 8·8, and that in the tartrate–phosphate titration about 10·4. The final potential of the platinum electrode indicated in the former titration should be − 0·50 volt, which was actually observed, whereas in the latter case, it should be − 0·61 volt, which is slightly more negative than that found. In a similar way the potentials assumed by the platinum electrode at the end of the acetate titrations can be shown to depend on the reaction $\mathrm{Cu}^{\cdot} \longrightarrow \mathrm{Cu}$ and the effect which p_H has on the solubility product of cuprous hydroxide.

WASHINGTON SINGER LABORATORIES, UNIVERSITY COLLEGE, EXETER.

[*Received, June 8th*, 1942.]