tillation should be continued. Picric acid may be substituted for platinum chloride, but the resulting crystals are not so characteristic. When no precipitate formed at once, examination under the microscope readily revealed whether more than mere traces of piperazine were coming over.

Another reagent giving characteristic crystals with piperazine is bismuth potassium iodide. The reagent is made by adding enough nitric acid to dissolve suspended bismuth nitrate and sufficient potassium iodide to give a clear red solution. Slight traces of piperazine salt in faintly acid solution give very brilliantly colored garnet crystals with a drop of this reagent. The form of the crystals varies from compact prisms to the more usual clusters of feathery needles. The double salt is very insoluble and it is hoped that it will offer a means of determining piperazine quantitatively.

A less delicate, but very definite, micro test for piperazine is the formation of dinitroso piperazine. A drop containing piperazine is acidified with hydrochloric acid in excess and flowed into a drop of saturated sodium nitrate solution. Slight warming gives characteristic, thin, rhombic, colorless plates.

The aqueous distillate, distinctly acid with hydrochloric acid, gave 366 g. of piperazine hydrochloride on evaporation to dryness. The crude salt may be recrystallized from dil. alcohol or converted into the free base by distilling from sodium hydroxide.

Anhydrous piperazine is a solid with distinctly caustic properties. For this reason it has been marketed in the form of various salts and as the hydrate.

It is sincerely hoped that the information here given may result in the manufacture of this greatly needed medicinal preparation by some American laboratory.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF MCGILL UNIVERSITY.]

THE COMPOUNDS OF PHENOL AND THE CRESOLS WITH PYRIDINE. II.

BY F. W. SKIRROW AND T. V. BINMORE.

Received June 21, 1918.

In a previous communication[1] by Mr. Hatcher and one of us, it was shown that the effect of excess of phenol in diminishing the extraction of pyridine from benzene solution by dil. sulfuric acid is much more marked than is the effect of excess of pyridine in diminishing the extraction of phenol by means of sodium hydroxide. The subsequent experiments were undertaken in order to elucidate this behavior.

It was shown by means of freezing-point curves that phenol forms two

[1] THIS JOURNAL, 39, 9, 1939 (1917).

compounds with pyridine, *viz.*, $C_6H_5OH.C_5H_5N$ and $(C_6H_5OH)_2.C_5H_5N$. A preliminary study was made of the dissociation of $C_6H_5OHC_5H_5N$ in benzene solution by means of cryoscopic measurements. This was complicated by the fact that phenol and to a lesser extent pyridine are associated in benzene solution, and that they as well as the undissociated pyridine phenate may be associated in the mixtures. As it is clearly impossible to evaluate all these factors from depression of freezing-point data alone, attempts were made to determine upper and lower limits for the degree of dissociation of the pyridine phenate by making plausible assumptions as to the simultaneous association taking place, and on these assumptions to calculate the degree of dissociation at different dilutions. It would perhaps be safer to speak of these values as the "apparent dissociation."

The assumptions made were 4 in number and as the same assumptions are used in the present paper they are here reproduced:

Assumption I.—The pyridine phenate dissociates into its constituents and no association of any kind follows.

Assumption II.—The pyridine phenate dissociates into its constituents and the constituents then associate as if each of them were alone in the solvent at the same concentration.

Assumption III.—As in II, except that the compound itself also associates in the same manner as the phenol in it would do if the whole of the phenol were alone in the solvent.

Assumption IV.—As in II, except that the compound itself also associates in the same manner as the pyridine in it would do if the whole of the pyridine were alone in the solvent.

It was shown that on any of these assumptions the apparent degree of dissociation of the pyridine phenate increases rapidly with increasing dilution.

Effect of Excess of the Constituents on the Apparent Dissociation.

In the present communication a study has been made of the effect of excess of phenol and of excess of pyridine on the apparent degree of dissociation of the pyridine phenate as determined by the cryoscopic method. the results being calculated on the same 4 assumptions as in the earlier paper. In all cases the determinations were made on an initial concentration of $C_6H_5OH.C_5H_5N$ of 3 cg. moles per 100 g. of benzene. To this were made, on the one hand, successive additions of phenol, and on the other hand, successive additions of pyridine. From the depression of freezing point of the benzene for each addition the apparent degree of dissociation was calculated. The method of calculation was similar to that employed in the earlier paper, making due allowance for the concentration of phenol or pyridine added in excess, so that the final equations only need be given, by the solution of which the dissociation was arrived at.

Let C = Concentration of $C_6H_5OH.C_5H_5N$ taken (in (Mols $\times 10^{-2}$ per) 100 g. of benzene).

D = Concentration of phenol or of pyridine added in excess (in the same units).

β = degree of dissociation of the compound at equilibrium.

C' = Initial concentration of the single molecules of the compound first produced by the dissociation of the assumed associated compound.[1]

N = Total number of solute molecules calculated from the depression of the freezing point.

α_1 = degree of dissociation of the associated phenol.

α_2 = degree of dissociation of the associated pyridine.

Equations:

Assumption I.—$N = C(1 + \beta) + D$.

Assumption II.—Here we have two sets of equations according to whether phenol or pyridine is in excess.

Phenol in excess.

$$N = C + C\beta/2\ (\alpha_1 + \alpha_2) + D/2\ (1 + \alpha_1)$$

where $\alpha_1 = 0.2313 - 0.0318\ (C\beta + D)$

and $\alpha_2 = 0.7378 - 0.008\ C\beta^2$

Pyridine in excess.

$$N = C + C\beta/2\ (\alpha_1 + \alpha_2) + D/2\ (1 + \alpha_2)$$

where $\alpha_1 = 0.2313 - 0.0318 C\beta$.

and $\alpha_2 = 0.7378 - 0.008\ (C\beta + D)$

These cases give a quadratic equation for one unknown.

Assumption III.—Phenol in excess.

$$C' = \frac{C\alpha_1}{1 + \alpha_1\beta - \beta}. \qquad (a)$$

$$N = C' + C'\beta/2\ (2\alpha_1 + \alpha_2 - 1) + C/2\ (1 - \alpha_1) + D/2\ (1 + \alpha_1) \qquad (b)$$

where $\alpha_1 = 0.2313 - 0.0318\ (C'\beta + D)$

and $\alpha_2 = 0.7378 - 0.008\ C'\beta$.

Pyridine in excess.

$$C' = \frac{C\alpha_1}{1 + \alpha_1\beta - \beta} \qquad (a)$$

$$N = C' + C'\beta/2\ (2\alpha_1 + \alpha_2 - 1) + C/2\ (1 - \alpha_1) + D/2\ (1 + \alpha_2) \qquad (b)$$

where $\alpha_1 = 0.2313 - 0.0318\ C'\beta$.

and $\alpha_2 = 0.7378 - 0.008\ (C'\beta + D)$

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[1] This is always eliminated in the solution of the simultaneous quadratic equations obtained.

[2] *Vide* earlier paper, *Loc. cit.*, p. 1950.

Assumption IV.—Phenol in excess.

$$C' = \frac{C\alpha_2}{1 + \alpha_2\beta - \beta}. \qquad (a)$$

$$N = C' + C'\beta/2\ (\alpha_1 + 2\alpha_2 - 1) + C/2\ (1 - \alpha_2) + D/2\ (1 + \alpha_1) \qquad (b)$$

where $\alpha_1 = 0.2313 - 0.0318\ (C'\beta + D)$

and $\alpha_2 = 0.7378 - 0.008\ C'\beta.$

Pyridine in excess.

$$C' = \frac{C\alpha_2}{1 + \alpha_2\beta - \beta}. \qquad (a)$$

$$N = C' + C'\beta/2\ (\alpha_1 + 2\alpha_2 - 1) + C/2\ (1 - \alpha_2) + D/2\ (1 + \alpha_2) \qquad (b)$$

where $\alpha_1 = 0.2313 - 0.0318\ C'\beta$

and $\alpha_2 = 0.7378 - 0.008\ (C'\beta + D).$

Assumptions III and IV yield simultaneous quadratic equations for C' and β between which C' is eliminated.

The foregoing equations reduce to the same as those quoted in the earlier paper by putting $D = 0$.

The results of these determinations are assembled in Table I and are shown graphically in Fig. 1.

In Table I Δ is the observed depression of freezing point with 3 cg. mols of $C_6H_5OH.C_5H_5N$ plus the excess of one constituent quoted per 100 g. of solvent, while the columns headed β_1, β_2, β_3, β_4 give the value of the degree of dissociation on Assumptions I, II, III and IV, respectively.

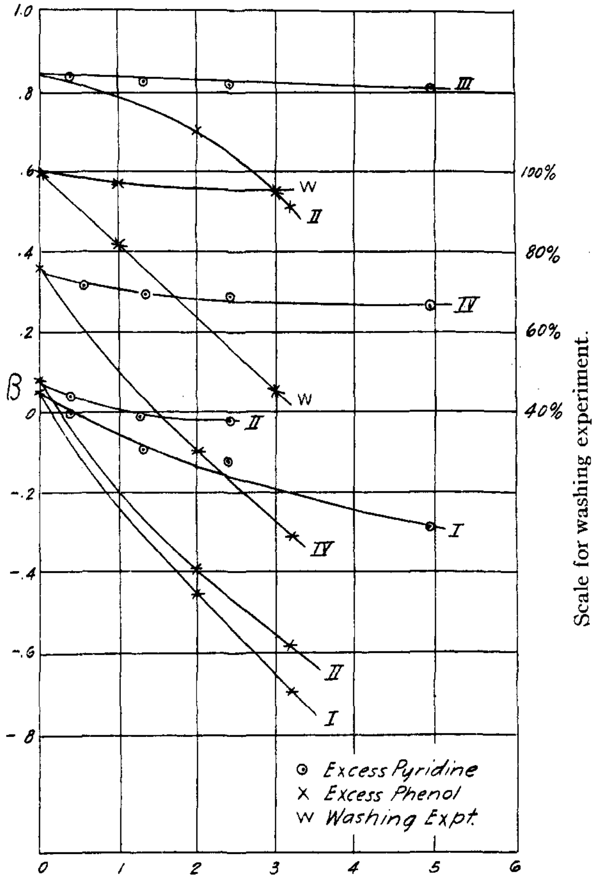
Table I.

	D.	Δ.	N.	β_1.	β_2.	β_3.	β_4.
Phenol in excess.....	0	1.555	3.110	0.0667	0.076	0.854	0.354
	2.003	1.827	3.654	—0.450	—0.386	0.709	—0.102
	3.172	2.034	4.068	—0.701	—0.578	0.514	—0.312
	5.148	2.363	4.726	—1.140	...	0.800	...
Pyridine in excess...	0	1.555	3.110	0.0667	0.076	0.854	0.354
	0.369	1.693	3.386	0.006	0.047	0.845	0.329
	1.307	2.069	4.138	—0.090	0.006	0.834	0.302
	2.412	2.526	5.052	—0.120	—0.014	0.829	0.297
	4.943	3.545	7.090	—0.284	...	0.813	0.268

The pairs of curves marked I, II, III, IV, in Fig. 1, are those obtained on Assumptions I, II, III, IV, respectively. It will be seen that it is immaterial which of these assumptions we make as to simultaneous association taking place; excess of phenol depresses the apparent dissociation of the pyridine phenate to a much greater extent than does excess of pyridine, and that the order of the difference is much the same on any of the assumptions. The pair of curves marked W are the results of extraction experiments included for comparison. The upper curve W represents the effect of excess of pyridine on the percentage extraction of phenol by means of sodium hydroxide, starting from the compound $C_6H_5OH.C_5H_5N$, while the lower curve W shows the effect of excess of phenol on the percentage extraction of pyridine by means of 2 N sulfuric acid, starting with the same compound. The similarity of the two effects in the extraction experiments to the two effects on the apparent degree of dissociation on any of the assumptions made will be at once apparent.

It should be remarked that in the extraction experiments the amount of acid or alkali used for extraction was the minimum amount which would just extract the whole of the phenol or pyridine in absence of the other constituent.

Dissociation of $C_6H_5OH.C_5H_5N$.



Excess phenol or pyridine.
(Mols × 10^{-2} per 100 g. of solvent.)
Fig. 1.

If we consider the scheme of dissociation postulated, *viz.*,

$$C_6H_5OH.C_5H_5N \rightleftarrows C_6H_5OH + C_5H_5N \text{ (Equilibrium 1)}$$

it will be obvious that the effect of excess of phenol should be the same as the effect of excess of pyridine, so that this cannot be the dominant equilibrium.

It was seen from the freezing-point curves that phenol and pyridine also form a second compound, $(C_6H_5OH)_2C_5H_5N$. It is conceivable that we have here to do with a dissociation,

$$(C_6H_5OH)_2.C_5H_5N \rightleftarrows 2C_6H_5OH + C_5H_5N \text{ (Equilibrium 2).}$$

In that case we should expect that if excess of pyridine were added the effect would be proportional to the concentration of the pyridine while if excess of phenol were added the effect would be proportional to the square of the concentration of the phenol.

It must be borne in mind, however, that the values of β are dependent on the scheme of dissociation postulated. A fresh series of determinations was therefore made, starting with the compound $(C_6H_5OH)_2.C_5H_5N$ at various concentrations in benzene and the values of the apparent degree of dissociation γ of this compound computed on the same set of assumptions as to simultaneous association as before. The effect of excess of either constituent on the value of γ was then studied for one initial concentration of $(C_6H_5OH)_2.C_5H_5N$ of 3 mols $\times$ 10^{-2} per 100 g. of benzene. These determinations involve a new set of equations for the calculation of γ, these equations being worked out on exactly similar lines to the equations for β, given in the earlier paper. The significance of the other symbols is the same as before.

Equations:

Assumption I.—$N = C(1 + 2\gamma) + D$.

Assumption II.—Phenol in excess.

$$N = C + C\gamma/2\ (1 + 2\alpha_1 + \alpha_2) + D/2\ (1 + \alpha_1)$$

where $\alpha_1 = 0.2313 - 0.0318\ (2C'\gamma + D)$

and $\alpha_2 = 0.7378 - 0.008\ C\gamma$.

Pyridine in excess.

$$N = C + C\gamma/2\ (1 + 2\alpha_1 + \alpha_2) + D/2\ (1 + \alpha_2)$$

where $\alpha_1 = 0.2313 - 0.0318 \times 2C\gamma$

and $\alpha_2 = 0.7378 - 0.008\ (C\gamma + D)$.

Assumption III.—In this case the values obtained with no excess of either constituent gave impossible values, rising rapidly far above unity, thus indicating that the actual number of solute molecules was greater than could be the case if the phenol in the compound retained its power to associate. The corresponding calculations with excess of the constituents were therefore omitted.

The equations with no excess present are as follows:

$$C' = \frac{C(1 - 2\alpha_1)}{2\gamma - 2\alpha_1\gamma - 1} \qquad (a)$$

$$N = C' - C'\gamma/2\ (1 - 4\alpha_1 - \alpha_2) + C\ (1 - \alpha_1) \qquad (b)$$

where $\alpha_1 = 0.2313 - 0.0318 \times 2C'\gamma$

and $\alpha_2 = 0.7378 - 0.008\ C'\gamma$

Assumption IV.—Phenol in excess.

$$C' = \frac{C\alpha_2}{1 + \alpha_2\gamma - \gamma} \qquad (a)$$

$$N = C' + C'\gamma\ (\alpha_1 + \alpha_2) + C/2\ (1 - \alpha_2) + D/2\ (1 + \alpha_1) \qquad (b)$$

where $$\alpha_1 = 0.2313 - 0.0318\,(2C'\gamma + D)$$
and $$\alpha_2 = 0.7378 - 0.008\,C'\gamma.$$

Pyridine in excess.

$$C' = \frac{C\alpha_2}{1 + \alpha_2\gamma - \gamma}. \qquad (a)$$

$$N = C' + C'\gamma\,(\alpha_1 + \alpha_2) + C/2\,(1 - \alpha_2) + D/2\,(1 + \alpha_2) \qquad (b)$$

where $$\alpha_1 = 0.2313 - 0.0318 \times 2C'\gamma$$
and $$\alpha_2 = 0.7378 - 0.008\,(C'\gamma + D)$$

The equations for the special case where no excess of either constituent above the amount required for $(C_6H_5OH)_2.C_5H_5N$ is present are obtained from the foregoing equations by putting $D = 0$.

The results obtained without excess of the constituents for various concentrations are given in Table II and are shown graphically in Fig. 2.[1]

C is the concentration of $(C_6H_5OH)_2.C_5H_5N$ taken.

Δ the observed depression of freezing point.

γ_1, γ_2, γ_3 and γ_4 the apparent dissociation on the various assumptions.

It will be seen that the values of γ on Assumption III lie entirely above unity, while in the other three cases the values fall regularly with increasing concentration and appear to be gradually tending to approach zero without becoming negative.

Dissociation of $(C_6H_5OH)_2C_5H_5N$.

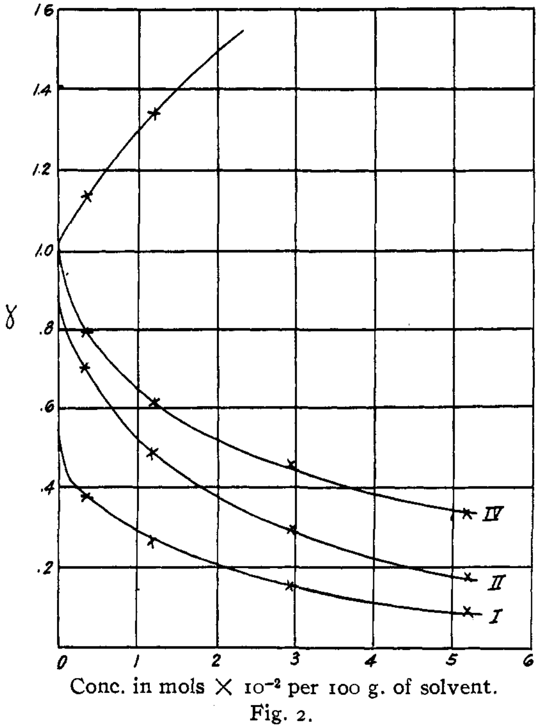


Fig. 2.

The results for the concentration of 3 cg. mols of the compound per 100 g. of benzene with various additions of each of the constituents in excess are shown in Table III and Fig. 3, the symbols having the same significance as before.

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[1] The depression of freezing-point data on which these are based were obtained last year by Mr. Hatcher but were not then worked up.

TABLE II.

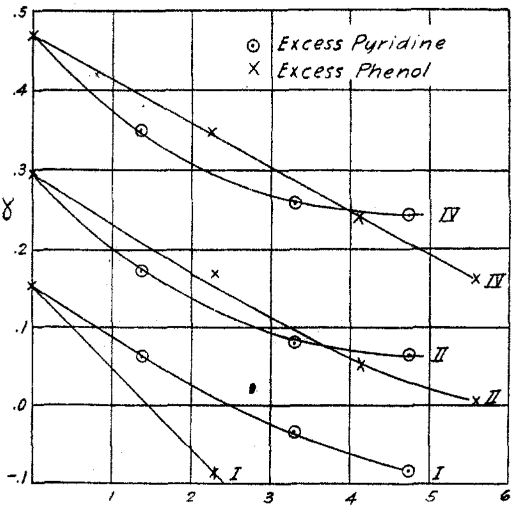
C.	Δ.	N.	γ_1.	γ_2.	γ_3.	γ_1.
0.186	0.176	0.352	0.446	0.833	..	...
0.240	0.227	0.454	0.446	0.829	..	...
0.338	0.296	0.592	0.375	0.695	1.14	0.785
0.619	0.507	1.014	0.319	0.596	..	...
0.758	0.606	1.212	0.300	0.564	..	...
1.217	0.919	1.839	0.256	0.482	1.34	0.616
1.681	1.211	2.422	0.220	0.421	..	...
2.002	1.403	2.806	0.201	0.384	..	...
3.002	1.970	3.940	0.156	0.301	1.75	0.467
3.672	2.326	4.652	0.133	0.258	..	...
4.364	2.680	5.360	0.114	0.221	..	...
5.237	3.114	6.228	0.095	0.183	2.30	0.344

TABLE III.

	D.	Δ.	N.	γ_1.	γ_2.	γ_4.
Pyridine in excess.............	0	1.960	3.920	0.153	0.295	0.467
	1.351	2.356	4.712	0.060	0.173	0.349
	3.289	3.038	6.076	—0.035	0.082	0.260
	4.729	3.610	7.220	—0.085	0.064	0.246
Phenol in excess...............	0	1.960	3.920	0.153	0.295	0.467
	2.310	2.399	4.798	—0.085	0.168	0.347
	4.134	2.698	5.396	—0.289	0.049	0.240
	5.581	2.976	5.952	—0.438	0.005	0.161

The pairs of curves corresponding to Assumption I both go below zero while those for Assumptions II and IV do not, up to the highest concentration used. But it will be seen that on these two assumptions the initial depressions in the value of γ caused by excess of pyridine are actually greater than those caused by excess of phenol. Only when nearly 4 cg. molecules excess of the constituents have been added does the depression caused by phenol exceed that caused by pyridine. A similar set of determinations were also carried out starting with 1 cg. mol of the compound and various amounts of the constituents in excess. The results were entirely similar to the foregoing and the curves

Dissociation of $(C_6H_5OH)_2C_5H_5N$.



Excess phenol or pyridine.
(Mols × 10^{-2} per 100 g. of solvent.)

Fig. 3.

of Fig. 3 could equally well be used to represent the results making the necessary alteration in the scale for γ.

It is thus evident that the dissociation

$$(C_6H_5OH)_2.C_5H_5N \rightleftharpoons 2C_6H_5OH + C_5H_5N$$

cannot be the dominant equilibrium and taken alone does not represent the facts.

It is possible, however, to explain both the extraction results and the two sets of dissociation determinations in the following way: Let us suppose that we start with the compound $C_6H_5OH.C_5H_5N$:

This dissociates in solution as follows:

$$C_6H_5OH.C_5H_5N \rightleftharpoons C_6H_5OH + C_5H_5N.$$

If we add excess of pyridine the effect in depressing the dissociation will be dependent directly on the concentration of the pyridine. If we add excess of phenol the effect in the first instance will similarly be dependent on the concentration of the phenol, but excess of phenol differs from excess of pyridine in that it promotes a second reaction.

$$C_6H_5OH.C_5H_5N + C_6H_5OH \rightleftharpoons (C_6H_5OH)_2.C_5H_5N \text{ (Equilibrium 3)}$$

and thus not only depresses the original dissociation in a normal way but also removes the compound $C_6H_5OH.C_5H_5N$ from the left hand side of that equilibrium, thus still further depressing the dissociation and removing the free pyridine from the system.

The system will thus contain not only free pyridine and phenol and their associated molecules but also will contain both compounds, $C_6H_5OH.-C_5H_5N$ and $(C_6H_5OH)_2.C_5H_5N$, to a greater or less extent.

The complete quantitative investigation of the equilibria involved is clearly impossible, on any assumptions as to association, by means of depression of freezing-point data alone. Further data would be necessary, such, for instance, as that which might be obtained if we had some solvent immiscible with benzene in which only one molecular species would distribute. The case is somewhat analogous to the dissociation of a dibasic acid where the hydrogen ion dissociates in two stages. In that case we have means of measuring the actual concentration of hydrogen ion.

It might be suggested that in this case we could get information as to the concentration of free pyridine from the extraction experiment, knowing the hydrolysis of pyridine sulfate, but, unfortunately, both phenol and pyridine phenate also dissolve in the aqueous layer, as shown in the earlier paper.

With large excess of pyridine, Equilibrium 1 probably represents the conditions fairly correctly, while with large excess of phenol Equilibrium 2 will be brought more to the fore. The reversal of Equilibrium 3 will probably be favored by increasing the dilution of the benzene solution.

Further Extraction Experiments.

In the experiments quoted in the earlier paper on washing out pyridine from benzene in absence of and in presence of phenol, the sulfuric acid employed was about 9.6 *N*, this being the concentration usual in works practice. As at this concentration the acid would be largely un-ionized, the experiments were repeated with more dilute acid. The result showed that as anticipated, much less acid was necessary to effect the complete removal of pyridine from pure benzene solution than when the more concentrated acid was employed.

As will be seen, the effect of addition of phenol on the extraction of the pyridine is still very much greater than was the effect of pyridine on the extraction of phenol by sodium hydroxide (see Fig. 1). The method was exactly the same as in the original experiments except that an improved procedure was adopted for the determination of the pyridine. As before the extracted pyridine sulfate was made alkaline with sodium hydroxide and distilled into excess of standard sulfuric acid, which was then titrated with standard sodium hydroxide, using methyl violet as indicator. The improvement consisted in utilizing a more sensitive method in determining the end-point. The solution was titrated directly to within about one cc. of the end-point and was then divided equally between two exactly similar Nessler tubes and the titration finished by running two drops of the standard alkali alternately into one tube and into the other until a point was reached when the addition of two drops gave a decided change compared to the tube which was two drops behind. Thus the point was not taken for the first slight change of nuance but for the point of maximum sensitiveness. In this way check experiments never differed by as much as 0.1 cc., and as the total amount of acid neutralized was of the order of 25 cc. this gives a satisfactory agreement considering the weak basic character of pyridine.

The standard solutions were standardized in the same manner against pure pyridine.

The acid used for extraction was made up roughly 2 *N* and its exact value in pyridine determined by direct titration.

1 g. pyridine = 6.26 cc. "Extraction acid."

This proportion is subsequently referred to as "theoretical acid."

Extraction of Pyridine from Benzene by 2 *N* Sulfuric Acid.—Five g. of pyridine was dissolved in benzene and made up to 100 cc. This was washed with "theoretical acid."

Pyridine extracted	99.5%

This is sufficiently close to the experimental error, so that theoretical acid was used for the extraction in presence of phenol.

In the previous experiments using 9.6 *N* acid it was necessary to employ 1.38 times theoretical acid to extract the pyridine completely from benzene solution of the same strength.

The results obtained in presence of phenol using the same concentration of pyridine and the same amount of acid for extraction are given in Table IV..

Effect of Dilution on the Extraction of Pyridine.

It has been seen that the apparent dissociation of the pyridine phenate compounds becomes greater and approaches unity as the concentration of the benzene solution becomes smaller. It would thus appear that the differences between excess of phenol and excess of pyridine should tend to disappear with greater dilution.

TABLE IV.

G. pyridine per 100 cc. solution.	Times theoretical acid.	Mols phenol per mol pyridine.	% extraction pyridine.
5	1.0	0	99.5
5	1.0	2	81.8
5	1.0	4	45.4
3	1.05	0	100.5
3	1.05	2	89.7
3	1.05	4	63.2
1	1.15	0	100.0
1	1.15	2	96.0
1	1.15	4	90.6

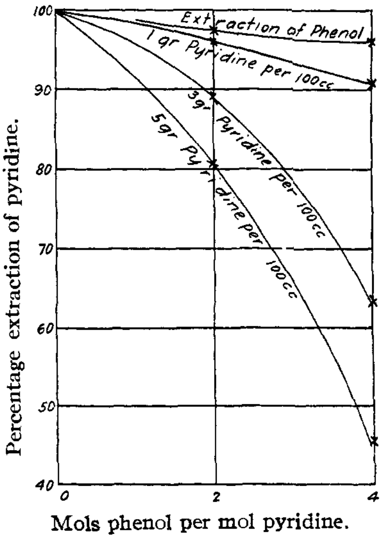


Fig. 4.

In order to check this point experiments were carried out on the extraction of pyridine in benzene solution in presence of phenol, using smaller initial concentration of pyridine. The same amounts of pyridine as before were taken and diluted to larger volumes before extraction. These results are also given in Table IV. Slightly more acid was needed for extraction of pyridine alone in the greater dilutions used.

It is thus evident that the above supposition is justified as the depression in the extraction caused by 4 molecules of phenol per molecule of pyridine is about 55% with a concentration of 5 g. per 100 cc. and about 9% with a concentration of one g. per 100 cc. This is better seen from Fig. 4, in which the extraction curve for phenol in presence of pyridine is also given, for a concentration of 5.95 g. phenol per 100 cc. solution. This would also be naturally somewhat higher at the lower concentrations, but this could not affect the general conclusion as the greatest diminution is only 5%.

The Cresols and Pyridine.—It was shown previously that in the case of *o*-cresol-pyridine only one compound, $C_7H_7OHC_5H_5N$, is formed and that in the case of *p*-cresol-pyridine two compounds are formed as with phenol. No complete freezing-point curves could be obtained with *m*-cresol-pyridine, so that no conclusions could be reached as to the compounds produced.

It is proposed to extend the extraction experiments to these cases, and also to study the effect of excess of the constituents on the dissociation of the compounds formed. It might be expected that with *o*-cresol-pyridine the effect of excess of pyridine or of the cresol would be the same in both these directions, while in the case of *p*-cresol we should get results similar to the case of phenol. It should be possible further in this way to obtain some information as to the compounds produced in the case of *m*-cresol-pyridine. This must be left to a subsequent communication.

Summary.

1. The effect of excess of phenol and excess of pyridine on the dissociation of pyridine phenate postulated as

$$C_6H_5OH.C_5H_5N \rightleftarrows C_6H_5OH + C_5H_5N$$

was studied by the cryoscopic method and it was found that phenol dedepressed the dissociation much more strongly than did pyridine.

2. This suggested that the dominant equilibrium might be

$$(C_6H_5OH)_2.C_5H_5N \rightleftarrows 2C_6H_5OH + C_5H_5N,$$

but a study of this dissociation on similar lines showed that the effect of excess of phenol on the apparent dissociation was only greater than the effect of excess of pyridine with comparatively high additions of these.

3. An explanation of these results and of the extraction results of the earlier paper is based on the following equilibria:

$$C_6H_5OH.C_5H_5N \rightleftarrows C_6H_5OH + C_5H_5N \qquad (a)$$

$$C_6H_5OH.C_5H_5N + C_6H_5OH \rightleftarrows (C_6H_5OH)_2.C_5H_5N \qquad (b)$$

4. It is shown that the difference between the effect of addition of excess of phenol and of excess of pyridine on the extraction experiments tends to disappear as the dilution of the benzene solution is increased.

MONTREAL, CANADA.