THE ADSORPTION ISOTHERM.

followed by

THE ACTION OF MONOCHLORMETHYLETHER ON AROMATIC AMINES.

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A. C. Brown.

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A reprint of this paper is affixed to the back cover.

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THE ADSORPTION ISOTHERM.

Part 1. — AT LOW AND INTERMEDIATE CONCENTRATIONS.

Part 1.

Adsorption at Low and Intermediate Concentrations.

Introduction.

The study of adsorption on a solid surface at a solid - liquid interface has been developed greatly in recent years, and much literature on the subject has been published.

The normal course in presenting the results is to make use of Freundlich's Empirical Formula for adsorption,

$$\frac{x}{m} = ac^{\frac{1}{n}},$$

where x is the amount adsorbed,

m is the amount of adsorbing substance,

c is the end concentration in solution,

a is an arbitrary constant, the value of which depends on the nature of the substances in question and the units used.

$\frac{1}{n}$, according to Freundlich, is always less than 1, generally between ·1 and ·5, but has a constant value for a given substance using the same adsorbent and solvent.

The graph log. $\frac{x}{m}$ (ordinates), log. c (abcissaè)
would then be a straight line, and, provided the same scale is chosen for ordinates and abcissaè, the gradient will equal $\frac{1}{n}$.

This equation has no theoretical foundation, but it is claimed that it is justified, as it fits the majority of experimental facts. An examination of some published data, to see how closely the formula interprets the experimental observations, is interesting.

Blitz (Ber., 1904, 37, 3138) and, more recently, Boswell and Dickson (J. Amer. Chem. Soc., 1918, 40, 1793) investigated the adsorption of arseneous acid by ferric hydroxide. The latter in their summary, state: " The logarithmic curves plotted from our measurements, although approximating to straight lines, yet show unmistakably a concavity to the x axis, thus indicating a deviation of the adsorption phenomenon from the adsorption equation ".

That is, over the relatively small range of concentration examined by them, they observed the value of $\frac{1}{n}$ to increase with decreasing concentration, its average value being about $\frac{1}{5}$.

Davis (J. 1907, 91, 1666) investigated the adsorption of iodine by different kinds of charcoal. The range of concentration examined is not very great, and an examination of the logarithmic curves for his results p.1681, indicates practically no deviation from the adsorption formula. It is significant, however, that the charcoal with the highest adsorptive power has also the lowest value for $\frac{1}{n}$.

Experimenting on the adsorption of dyes in very dilute solution by cotton fibres, Georgievics observed that $C_{fibre}/C_{solution}$ is a constant (Zsigmondy "Chemistry of Colloids" 1917, p.205),that is, the value of $\frac{1}{n}$ is 1. Again, the same author (Monatsh 1913, 34, 733) states that the interpretation of the meaning of x in the ordinary distribution formula,

$$\sqrt[x]{C_1}/C_2 = K ,$$

has hitherto been a matter of difficulty; when the range of concentration varies greatly,it is often necessary to have different values of x for different ranges of concentration,in order to obtain a constant value for K . That is, using the empirical formula to interpret the results, the value of $\frac{1}{n}$ changes with alteration in concentration. Williams (Medd. K.Vet. Nobelinstitut 1913, 2. No.27, 1-23), working on the adsorption of acetic acid by blood charcoal finds that his results seem to show that, for very great dilutions, $\frac{1}{n}$ becomes a whole number or a simple fraction.

Carrying out some absolute measurements of coefficients of adsorption, Bancelin (Compt.rend. 1914, 158, 791) observed that the adsorption of dyes and also of sodium chloride by glass plates increased with the concentration, but was not exactly proportional to it. That is, the value of $\frac{1}{n}$ was a little less than 1.

Summarising the foregoing data, the value of $\frac{1}{n}$ appears to equal 1 for very dilute solutions, but there is difficulty in proving this quantitatively for such low concentrations by the methods employed. For solutions of intermediate concentration, the value of $\frac{1}{n}$ is less than 1, and tends to decrease with increasing concentration.

The study of the adsorption of radio-active substances is a valuable aid to the investigation of the phenomenon at very low concentrations, as the amount of radio-active substance present can be accurately measured, when present in very much smaller amount that the limits of chemical or other physical means. One is thus enabled to study adsorption at that most interesting stage when the first layer of atoms or molecules is being laid down. Berry (J.1910, 97, 196) investigated the adsorption of uranium X by precipitation of barium sulphate in a solution of uranium nitrate. The claim is made that the value of $\frac{1}{n}$ (n in Berry's paper) is scarcely affected by diminishing concentration of uranium X. In his calculations, however, the constant "a" of the adsorption equation is omitted, and the calculation of $\frac{1}{n}$ is thus vitiated. On graphing log. $\frac{x}{m}$, log. c for the figures given, no definite value can be ascribed to the exponent, its value, however, appears to be greater than unity which is contrary to the accepted views on adsorption. More recently, Ebler and Rhyan (Ber., 1921, 54, 2896) carried out similar experiments by precipitating barium sulphate, in increasing quantity, by sulphuric acid, in a solution of barium and radium chlorides. They obtained for log. $\frac{x}{m}$, log. c a curve, convex to the x axis, and the value of $\frac{1}{n}$ appears to increase, with increasing concentration, from a small fraction up to approximately 1. They omit, however, to take into consideration that, as shown by Berry's work on uranium X, the value of "a" is probably altered by alteration of the hydrogem ion concentration, so that the graph doesnot represent the path of adsorption under constant conditions.

Ritzel (Z. physikal. Chem. 1909, 67, 724) investigated the adsorption of uranium X by charcoal,and found the value of the exponent $\frac{1}{n}$ to be 1. He also observed that the addition of a trace of thorium prevents the adsorption of uranium X.

Soddy (J. 1911, 99, 72) believes that the prevention of the adsorption of uranium X by thorium is connected with the isotopism of the two elements.

Freundlich, Newmann and Kaempfer (Physikal Zeitsch 1914,15,537) in a paper on the "Influence of the presence of other substances on the adsorption of Uranium X" disagree with Soddy's explanation. Their argument is, that while thorium nitrate prevents the adsorption of uranium X , other substances, zirconium salts and even benzoic acid have an appreciable effect. In another paper on the same subject,Freundlich and Kaempfer (Z. physikal Chem.1915, 90, 681) reaffirm their views. They also found the adsorption coefficient for both uranium X and thorium nitrate both nearly unity.

Now, if it is accepted that uranium X and its isotope thorium are not separable by an adsorption process, an assumption justified by the work of Fleck (J.1913,103, 381), and also, if is accepted that the adsorption coefficient of uranium X is 1, then the value for $\frac{1}{n}$ must decrease with increasing concentration of the hetratope "atomic number 90", because if it remained equal to 1, increasing concentration, brought about by the addition of thorium, would not alter the ratio of the amount of hetratope adsorbed to that in solution in equlibrium, and the β activity of the adsorbent (a measure of the amount of uranium X present) would remain unaltered.

It occurred to the author that, by making use of the isotopy of uranium X and thorium, one could follow the course of adsorption uniformly from very low concentrations up to the point of saturation, and, with the view of observing the alteration in the value of $\frac{1}{n}$, the following series of experiments were carried out:-

1. Investigation of the adsorption of uranium X from solutions containing no thorium.
2. Investigation of the adsorption of uranium X from

solutions containing known small concentrations of thorium.

Uranium acetate was used as the source of uranium X, and basic ferric acetate as the adsorbent.

Experimental.

After many preliminary experiments, it was found best to use basic ferric acetate as adsorbent. A few drops of a ferric sulphate solution were added to a boiling solution of uranium acetate, the acidity of which had been previously adjusted, and boiled under a reflux condenser for 30 minutes. On boiling for a larger period, no alteration in the amount adsorbed was observed. It was noticed that if the iron solution was added in the cold, less uranium X was adsorbed. This was probably due to the colloidal particles in the latter case being larger.

The advantages of this procedure were that the conditions were quite standard and, moreover, after filtration, the solution was practically unchanged.

Preparation of Iron Sulphate Solution.

12·5 grams anhydrous ferric sulphate were dissolved in 250 c.c. water with the addition of a little sulphuric acid to prevent hydrolysis. 1 c.c. of this solution was taken as unity in the determination of m.

Preparation of Uranium Acetate Solution.

28 grams uranium acetate, $UO_2(CH_3COO)_2.2H_2O$, were dissolved in 600 c.c. water and 35 c.c. of sulphuric

acid (10 gms. per 100 c.c.), 17·5 c.c. of sodium acetate soln. (30 gms. per 100 c.c.) were then added, and the solution boiled under a reflux condenser for 30 minutes. The flocculent matter which appeared was filtered off and the volume made up to 700 c.c.

Estimation of Total β Activity.

20 c.c. of this solution were diluted with 50 c.c. water, and 5 drops of a thorium nitrate solution (1 c.c. = 0·08 gram of thorium) added. After mixing, 0·5 gram of ammonium benzoate was added, and the solution boiled under reflux for five minutes. The precipitate of thorium benzoate was immediately filtered off by suction on a double layer of ash-free filter paper, about 1¼" diameter, supported on a porcelain plate. This was the method adopted for all subsequent filtrations.

This treatment removed about 98% of the uranium X.

A further treatment with 5 drops of thorium solution removed the remainder.

The β activities of these precipitates, and also of the flocculent matter were observed, corrections were made for decay between time of precipitation and observation, and the readings standardised by comparison with a standard of Uranium Oxide.

β activity of flocculent matter = 67·48 div.per min.
" " first ppt. = 10·80
" " second ppt. = $\underline{0{\cdot}22}$
" of 700 c.c.soln. 11·02 x 35 = $\underline{385{\cdot}70}$
453·18 " " "

This is the β activity due to uranium X when present in equilibrium quantity.

Removal of Thorium if present.

The clear solution (680 c.c.) was raised to boiling under a reflux condenser, and 1 c.c. of the iron solution was added. After boiling for 30 minutes, the solution was filtered hot. Scarcely any iron was precipitated owing to its slight solubility. A further 1 c.c. of iron solution was now added to the boiling solution, which was again boiled for 30 minutes and filtered, and a precipitate was now obtained.

The treatment with iron was repeated 16 times. This removes any thorium which might be present together with all the uranium X. The solution was made up to the original volume (680 c.c.) and left for several weeks to generate uranium X.

Series 1. Thorium Absent.

560 c.c. of the solution were placed in a round bottomed litre flask and brought to boiling under a reflux condenser. 5 drops of the iron solution were added, the solution boiled for 30 minutes, and the precipitate of basic ferric acetate filtered off. This treatment with 5 drops iron solution was repeated six times. The β activities of these precipitates were observed.

The total β activity due to uranium X was obtained by calculation from the decay curve and checked by a determination on a fresh quantity of the original solution. The equilibrium activity after each precipitation was obtained by difference, the amount of uranium X regenerated between experiments being taken into account; this was most important towards the end of the series. The amount of adsorbent was determined with $\frac{N}{200}$ titanous chloride.

The results are given in Table 1 and the graph log. $\frac{x}{m}$, log. c in Fig. 1.

m = amount of adsorbent (1 c.c. iron soln.= 1)

x = β activity of adsorbent in div.per min.

c_1 = equilibrium β activity in solution (560 c.c.)

c = " " " per 100 c.c.

The total β activity of 560 c.c. solution at the start was 289·87 div.per min.

TABLE 1.

Series. 1. Thorium Absent.

EXP. NO.	m.	X.	C_1	C	LOG $\frac{X}{m}$.	LOG C.
1.	·246	180·16	109·8	19·60	2·865	1·292
2.	·255	71·84	38·02	6·79	2·450	·832
3.	·231	25·81	12·43	2·22	2·048	·346
4.	·222	8·20	4·45	·794	1·568	$\bar{1}$·900
5.	·164	2·85	1·92	·343	1·240	$\bar{1}$·535
6	·192	1·36	·80	·143	·850	$\bar{1}$·185
7.	·681 (15 drops)	1·10	——	——	·207	——

The results obtained were fully confirmed by repetition.

Series. 11. Thorium Added.

The solution which had been used for Series. 1. was, after keeping for some weeks, used for this series also.

The amount of uranium X corresponding to 1 div.per min. β activity was calculated and found to be 0·407 x 10^{-12} gram.

1 c.c. of thorium nitrate solution was found to contain 0·07575 gram of thorium. The same number of atoms of uranium X would weigh 0·07513 gram , and would give a β activity of $1{\cdot}846 \times 10^{11}$ div.per min.

By successive dilution, solutions of thorium were prepared ranging down to concentrations comparable with that of the uranium X solution. The procedure was to add the desired amount of thorium (contained in 1 c.c. water) to 50 c.c. of the uranium X solution of known strength and to heat the mixture to the boiling point. 10 drops of an iron solution of one fifth the original strength were then added, and after boiling 30 minutes,the precipitate was filtered off and the β activity and iron determined.

The first addition of thorium was equivalent to 0·2 c.c. of the original thorium nitrate solution,which corresponds with the number of atoms of uranium X giving a β activity represented by $3{\cdot}69 \times 10^{10}$ div. per min.

50 c.c. of the uranium X solution had a β activity represented by 24·78 div. per min. so that the concentration of the hetratope "atomic number 90" was raised by the factor $1{\cdot}49 \times 10^{9}$.

The results are recorded in Table 11, and depicted in the graph log. $\frac{x}{m}$, log. c shown in Fig.11.

The part of the latter enclosed by the rectangle A.B.C.D. is Fig. 1, on the reduced scale.

T = c.c. of the original thorium nitrate soln.added.
x_1 = β activity of adsorbent in div.per min.
x = hetratope "atomic number 90" on adsorbent in div. per min.
m = amount of adsorbent (1 c.c. original iron soln.= 1)
c_1 = β activity in div. per min. in filtrate (560 c.c.), in equilibrium.
c = hetratope "atomic number 90" per 100 c.c. of filtrate in div. per min. in equilibrium.

The solubility limit was exceeded when $T = 2$, and a precipitate appeared on boiling. By observing the activity of this precipitate, the solubility limit shown in Fig.11 , was obtained by calculation. It corresponded with 0·17 per cent of thorium.

TABLE. 11. (Series 11. Thorium Added.)

EXP. NO.	T.	x_1.	x.	m.	C_1.	C.	LOG $\frac{x}{m}$.	LOG C.
1	—	21·50	21·50	·062	3·28	6·58	2·5195	·817
2	·2	2·27	$2{\cdot}27 \times 1{\cdot}49 \times 10^9$	·042	22·51	$45{\cdot}02 \times 1{\cdot}49 \times 10^9$	10·906	10·827
3	·02	8·88	$8{\cdot}88 \times 1{\cdot}49 \times 10^8$	·059	15·90	$31{\cdot}80 \times 1{\cdot}49 \times 10^8$	10·352	9·676
4	$\cdot 0_3 2$	17·10	$17{\cdot}10 \times 1{\cdot}49 \times 10^6$	·055	7·68	$15{\cdot}36 \times 1{\cdot}49 \times 10^6$	8·666	7·360
5	$\cdot 0_5 2$	22·03	$22{\cdot}03 \times 1{\cdot}49 \times 10^4$	·076	2·75	$5{\cdot}50 \times 1{\cdot}49 \times 10^4$	6·636	4·914
6	$\cdot 0_7 2$	21·70	$21{\cdot}70 \times 1{\cdot}49 \times 10^2$	·080	3·08	$6{\cdot}16 \times 1{\cdot}49 \times 10^2$	4·606	2·963

The results were confirmed by repetition.

TABLE. 111.

	SERIES I.			SERIES II.							
LOG. $\frac{x}{m}$	1	2	3	4	5	6	7	8	9	10	11
$\frac{1}{n}$ ……	0·97	0·97	0·96	0·96	0·97	0·97	0·92	0·87	0·77	0·65	0·44

← LIMIT OF ANALYSIS BY CHEMICAL MEANS.

FIG. 1.

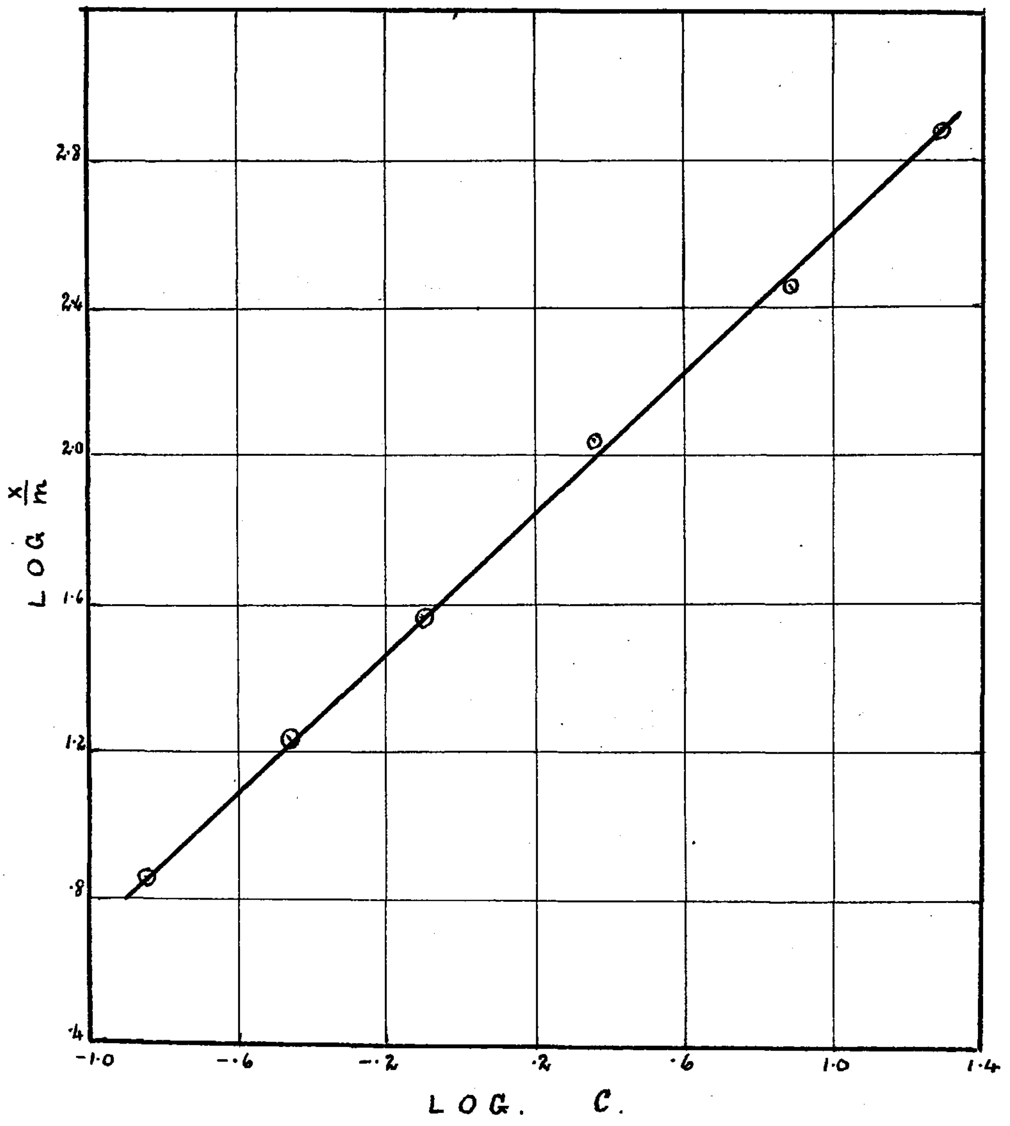
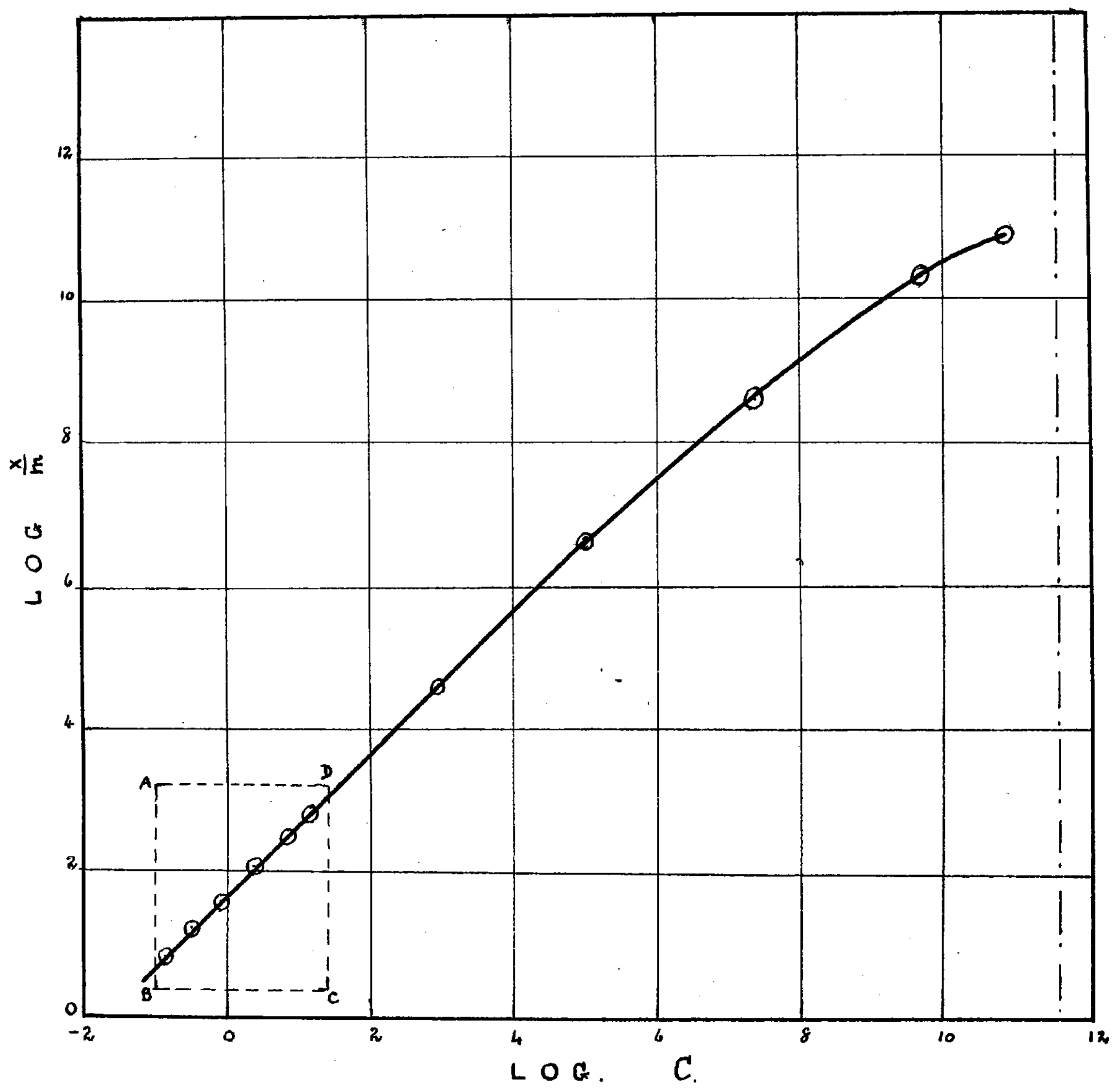


FIG. 11.



———·———·——— = SOLUBILITY LIMIT

Results and Discussion.

For the adsorption of uranium X in absence of thorium, the exponent $\frac{1}{n}$ was found to be 1. (Fig.1.). With the addition of its isotope, this value was at first not affected, then, with increasing concentration, the value of $\frac{1}{n}$ decreased (Fig.11.), the calculation of course being based on the assumption that the thorium is divided between adsorbent and solution in the same ratio as the uranium X. The values of $\frac{1}{n}$ for the respective logarithms of the concentration on the adsorbent ($\frac{x}{m}$) are shown in Table 111.

At the limit of chemical means of investigation, indicated roughly by the arrow in Table 111, the value of $\frac{1}{n}$ is already well below 1.

This seems to indicate that at first the potential capacity of the adsorbing surface does not alter, but, with increasing surface concentration, after a certain point it becomes weaker and weaker. Thus, for very small surface concentrations, the value of the exponent will be independent of the nature of the adsorbent, solvent, or adsorbed substance and will equal 1, but with increasing surface concentration the value of the exponent will fall, andthe greater the surface concentration the smaller will be the value of $\frac{1}{n}$, other factors being constant. The inability to measure the surface of the adsorbent used prevents any conclusions being drawn as to the thickness of the surface layer, but the general inferences are in agreement with Langmuir's experimental results and theoretical deductions on the adsorption of gases at surfaces of known area (J. Amer.Chem.Soc.,1918,40,1361). Since the value of the exponent continually decreases, once it has become less than 1, Freundlich's adsorption law is strictly true only when $\frac{1}{n} = 1$ (Hendry's law). When $\frac{1}{n}$ is less than 1,the law is an approximation holding only over relatively small ranges of concentration. This explains the slight deviations observed by Boswell and Dickson and others, and shown by the concavity of their graphs to the x axis. On the other hand, the slow rate of change of value of $\frac{1}{n}$ with increasing concentration accounts for the constant, fractional values sometimes obtained in the investigation of adsorption phenomena; Freundlich and Masius (Gedenboek aangeboden ann J.M. Van Bemmelen 1910, 88-101) quote some values of $\frac{1}{n}$ to 4 decimal places. Returning to a consideration of the different explanations of the prevention of the adsorption of uranium X by thorium offered by Soddy, and by Freundlich and his colleagues, it will be evident that Soddy's explanation requires also, that the amount of thorium present will be sufficient to cause the adsorption coefficient of the hetratope to be less than 1. In the case of Freundlich and his colleagues' argument, it is hard to reconcile the two statements that, while they found thorium to prevent the adsorption of uranium X, they also found the coefficients of adsorption for both uranium X and thorium nitrate to be nearly unity.

Summary.

1. The adsorption of uranium X by basic ferric acetate is proportional to the concentration, and thus, the exponent $\frac{1}{n} = 1$.
2. By "artifically" increasing the concentration of uranium X by the addition of its isotope, thorium, the value of $\frac{1}{n}$ is at first unchanged, but with increasing concentration its value decreases.
3. The fall in the value of the exponent with increasing concentration is in general agreement with Langmuir's theoretical deductions on the adsorption of gases at solid surfaces.
4. The decreasing value of the exponent offers an explanation of the deviations observed by Boswell and Dickson.
5. The decreasing value of the exponent offers an explanation of the experimental observation that a trace of thorium prevents the adsorption of uranium X.
6. Freundlich's adsorption law is strictly true only when the exponent equals 1 (Hendry's law). For values less than 1, the law is only approximate, and the comparative constancy of the exponent observed by other investigators can be explained by the relatively small ranges of concentration over which their observations were made.

THE ADSORPTION ISOTHERM.

Part 11.— AT THE SOLUBILITY LIMIT.

Part 11. The Adsorption Isothermat the Solubility Limit.

The course of adsorption,from very dilute solution up to moderate concentration,is described in detail in Part 1, and it seemed of interest to follow its course till the point of saturation was reached.

The method adopted was similar to that previously employed, the isotopy of uranium x and thorium being again used as a means to this end.

Slight modifications in the procedure were introduced where necessity arose, these are described in the experimental section.

All radioactive measurements were,as before,corrected for the natural leak of the electroscope, and the decay between time of precipitation and measurement. The readings were finally standardised by comparison with a standard of black uranium oxide.

Experimental.

Preparation of Iron Sulphate Solution.

12.5 grams of anhydrous ferric sulphate were dissolved in 250 c.c. of water with the addition of a little sulphuric acid to prevent hydrolysis. One c.c. of this solution was taken as unity in the determination of m. This solution is of the same strength as that used in Part 1.

Preparation of Uranium Acetate Solution.

32 grams of uranium acetate, $UO_2(CH_3O_2)_2 \cdot 2H_2O$, were dissolved in 600 c.c. distilled water and 40 c.c. of dilute sulphuric acid (10 grams per 100 c.c.). 20 c.c. of sodium acetate solution (30 grams per 100c.c.) were then added, and the solution boiled under reflux for 30 minutes. A slight flocculent precipitate, which appeared, was filtered off and the volume made up to 640 c.c.

40 c.c. of this solution, equivalent to 50 c.c. of the solution employed in Part 1, were taken for each experiment, and the volume made up to 50 c.c. after the addition of the requisite amount of thorium nitrate solution. The undiluted solution will subsequently be referred to as the "original uranium acetate solution".

Thorium Nitrate Solution.

A solution, found by analysis to contain 0.07575 gram of thorium per c.c., was employed. This is the same as that used in Part 1.

Estimation of Total β Activity.

The following method, simpler than the thorium benzoate method employed in the previous experiments, was used. 40 c.c. of the original uranium acetate solution were brought to boiling, under reflux, and one c.c. of iron solution added. The mixture was boiled for half an hour, and the precipitated basic ferric acetate filtered off. This precipitate contained more than 90% of the uranium X. A further treatment with one c.c. of iron solution was carried out, and the precipitate filtered off on the same filter paper. The united precipitates contained more than 99% of the uranium X originally present.

40 c.c. original uranium acetate solution =

9.13 div. per min. β activity.

Determination of the Solubility Limit.

This point is roughly indicated in Part 1, but, for the purposes of these experiments, it required to be accurately known.

As time was necessary for complete precipitation, the following experiment was first performed. Four c.c. of thorium nitrate solution were added to 40 c.c. of original uranium acetate solution, and the volume made up to 50 c.c. The mixture was refluxed for half an hour, and the white precipitate, which appeared, was filtered off. On again boiling the filtrate, a further precipitate appeared. It was found that precipitation was complete after boiling two hours, but to ensure this, a minimum of four hours boiling was given in all subsequent experiments.

A mixture, containing the same quantities of thorium nitrate and uranium acetate, was again prepared, and boiled under reflux for four hours. The precipitate waa filtered off, and the β activity determined.

β activity of precipitate = 5.49 div. per min.

β activity of 40 c.c. original uranium acetate solution = 9.13 div. per min.

β activity of solution in equilibrium (by difference.)
3.64 div. per min.

Thus, the solubility limit is reached when

$$\frac{3.64}{9.13} \times \frac{4}{1} = 1.6 \text{ c.c. of thorium nitrate}$$

solution is added to 40 c.c. of original uranium acetate solution, and the volume made up to 50 c.c.

Examination of Precipitate.

Though the chemical composition of the thorium compound precipitated is of little importance, it seemed of interest to examine it. A quantity was prepared by the method described above, filtered off, and washed with a little boiling water to remove any adhering mother liquor. It was then air dried.

0.2660 gram on ignition gave 0.1816 gram ThO_2 = 68.27 % ThO_2.
0.3474 gram gave 0.1478 gram $BaSO_4$ = 14.60 % SO_3.
Water (by difference) = 17.13 % H_2O.

testing for the presence of acetate gave negative results.

The analysis corresponds to $7ThO_2 \cdot 5SO_3 \cdot 26H_2O$, a hydrated basic sulphate of thorium, further investigation of this, however, was not made.

Adsorption Experiments.

Suitably diluted solutions of the original thorium nitrate solution were prepared, so that 0.2 c.c., 0.4 c.c., 0.8 c.c., and 1.6 c.c. respectively, were contained in two c.c. of water. Two c.c. of the first of these solutions were added to forty c.c. of original uranium acetate, the volume made up to 50 c.c., and the solution raised to boiling. One c.c. of iron solution was added and the mixture boiled under reflux for four hours. The precipitate of basic ferric acetate was then filtered off, and the β activity measured. Identical experiments were carried out employing two c.c. of the other three prepared thorium nitrate solutions.

The last of these experiments represents the case for a saturated solution, but it was thought advisable to make some observations beyond this point.

4 c.c. of the original thorium nitrate solution were added to 40 c.c. of original uranium acetate solution, the volume made up to 50 c.c., and the solution heated to boiling. A white precipitate of basic thorium sulphate began to appear, but, neglecting this, one c.c. of iron solution was added, the solution boiled under reflux for four hours, the precipitate filtered off, and the β activity measured.

This was repeated using 7 c.c. of the original thorium nitrate solution.

In each case the iron was estimated by means of $^{N}/_{200}$ titanous chloride solution, one c.c. of the iron sulphate solution being taken as unity in the calculation of m.

The results, in tabular form, are shown in Table A, and the graph Log $\frac{x}{m}$, Log C , is depicted in Fig.A.

m = amount of adsorbent (1 c.c. of iron solution = 1).

T = c.c. of the original thorium nitrate solution added.

x_1 = β activity of adsorbent in div. per min.

x = amount of thorium on the adsorbent calculated as β activity, in div. per min.

c_1 = β activity, in div. per min. in the filtrate (50 c.c.) in equilibrium.

c = amount of thorium per 100 c.c. of filtrate in equilibrium calculated as β activity in div.per min.

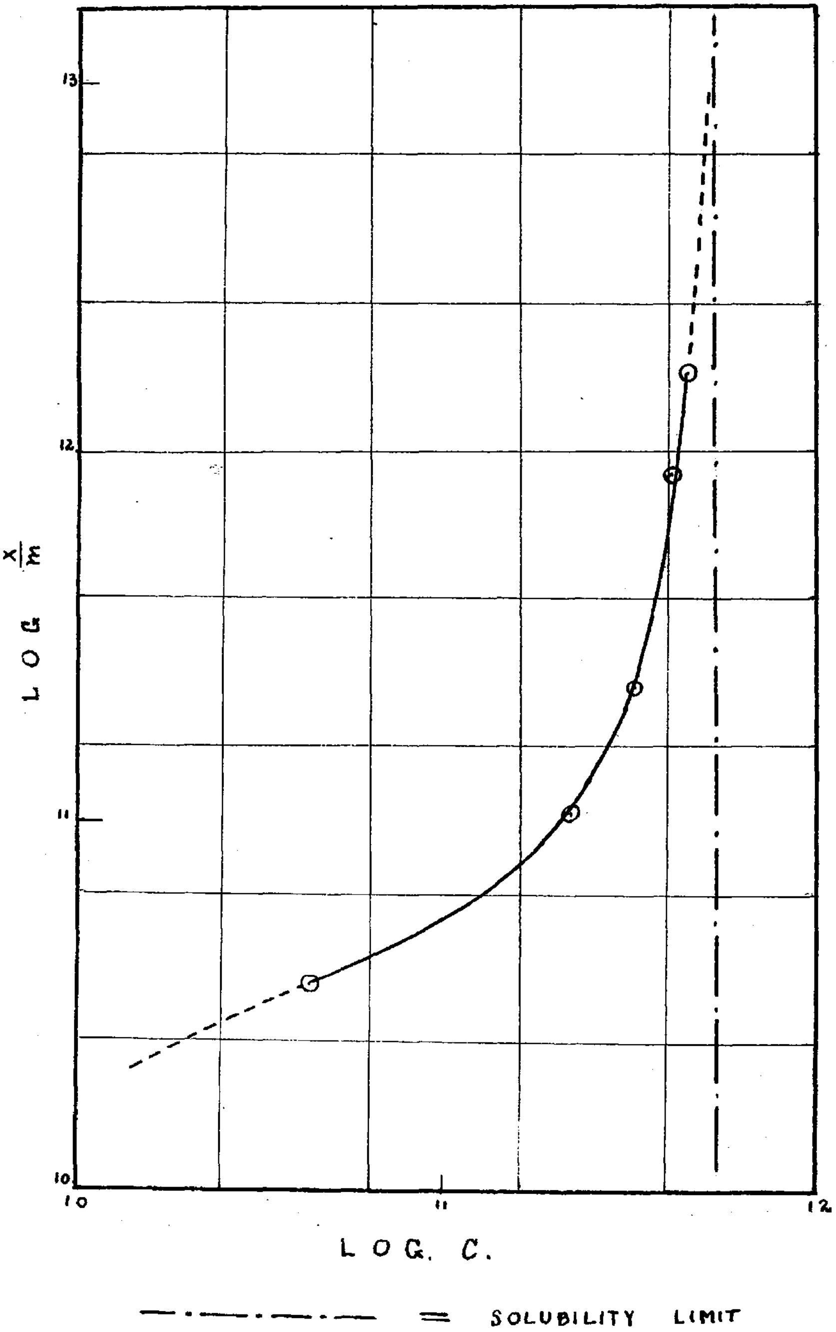
In place of the factorial method employed in Part 1, of converting the hetratope "atomic number 90" to β activity in div. per min., the ratios of the β activities of the precipitates, to the β activities in solution in equilibrium, were taken as the ratios of thorium adsorbed, to that in solution in equilibrium. This method of calculation is quite accurate, as, for this series of experiments, the amount of uranium X is negligible compared with the amounts of thorium present.

In Part 1, one c.c. of thorium nitrate solution, containing 0·07575 gram of thorium is shown to correspond to a β activity of $1{\cdot}846 \times 10^{11}$ div. per min. A simple calculation thus suffices to transform the amounts of thorium adsorbed, and in equilibrium, into β activity in div. per min.

TABLE. A.

EXP. NO.	T	X_1	m	$\frac{x}{m}$	C_1	C	LOG $\frac{x}{m}$	LOG C
1.		9·13						
2.	0·2	3·74	0·42	$\frac{3{\cdot}74\times1{\cdot}846\times10^{11}\times0{\cdot}2}{0{\cdot}42\times9{\cdot}13}$	5·39	$\frac{2\times5{\cdot}39\times1{\cdot}846\times10^{11}\times0{\cdot}2}{9{\cdot}13}$	10·5524	10·6393
3.	0·4	3·57	0·46	$\frac{3{\cdot}57\times1{\cdot}846\times10^{11}\times0{\cdot}4}{0{\cdot}46\times9{\cdot}13}$	5·56	$\frac{2\times5{\cdot}56\times1{\cdot}846\times10^{11}\times0{\cdot}4}{9{\cdot}13}$	10·7187	10·9539
4	0·8	1·76	0·34	$\frac{1{\cdot}76\times1{\cdot}846\times10^{11}\times0{\cdot}8}{0{\cdot}34\times9{\cdot}13}$	7·37	$\frac{2\times7{\cdot}37\times1{\cdot}846\times10^{11}\times0{\cdot}8}{9{\cdot}13}$	11·0228	11·3373
5	1·6	3·34	0·49	$\frac{3{\cdot}34\times1{\cdot}846\times10^{11}\times1{\cdot}6}{0{\cdot}49\times9{\cdot}13}$	5·57	$\frac{2\times5{\cdot}57\times1{\cdot}846\times10^{11}\times1{\cdot}6}{9{\cdot}13}$	11·3562	11·5167
6	4·0	6·66	0·63	$\frac{6{\cdot}66\times1{\cdot}846\times10^{11}\times4{\cdot}0}{0{\cdot}63\times9{\cdot}13}$	2·46	$\frac{2\times2{\cdot}46\times1{\cdot}846\times10^{11}\times4{\cdot}0}{9{\cdot}13}$	11·9313	11·6033
7	7·0	7·55	0·67	$\frac{7{\cdot}55\times1{\cdot}846\times10^{11}\times7{\cdot}0}{0{\cdot}67\times9{\cdot}13}$	1·58	$\frac{2\times1{\cdot}58\times1{\cdot}846\times10^{11}\times7{\cdot}0}{9{\cdot}13}$	12·2027	11·6505
SOLUBILITY LIMIT						$\frac{2\times3{\cdot}64\times1{\cdot}846\times10^{11}\times4{\cdot}0}{9{\cdot}13}$		11·7299

FIG. A.



Discussion of Results.

As the concentration increases, the value of $\frac{1}{n}$ passes through a minimum, then rapidly increases to infinity. This tendency to increase is noticeable long before the initial solution is saturated (Exp. 5), being quite marked when the quantity of thorium nitrate present is only half that necessary to produce a saturated solution (Exp. 4). In the final experiment, the equilibrium concentration is still slightly below the normal saturation value, although the initial concentration was much above that value.

From the shape of the graph, we may infer that some force, negligible at low concentrations, rapidly comes into prominence as the solubility limit is approached, tending to augment the adsorption effect. This is undoubtedly the attraction between the adsorbed substance, and that in solution - the mutual attraction, which normally brings about crystallisation. Crystallisation can be regarded as a special case of adsorption; when a crystal surface is in contact with a solution of the same substance in super-saturated solution, adsorption at the crystal face proceeds till equilibrium is attained - the point of saturation. Crystallisation is, however, a special case of adsorption, in that the new surface continually forming, retains the original adsorptive power unimpared, and the equilibrium concentration, as a result, is a constant, no matter what degree of supersaturation was originally present.

If we apply the adsorption equation

$$\frac{x}{m} = a c^{\frac{1}{n}}$$

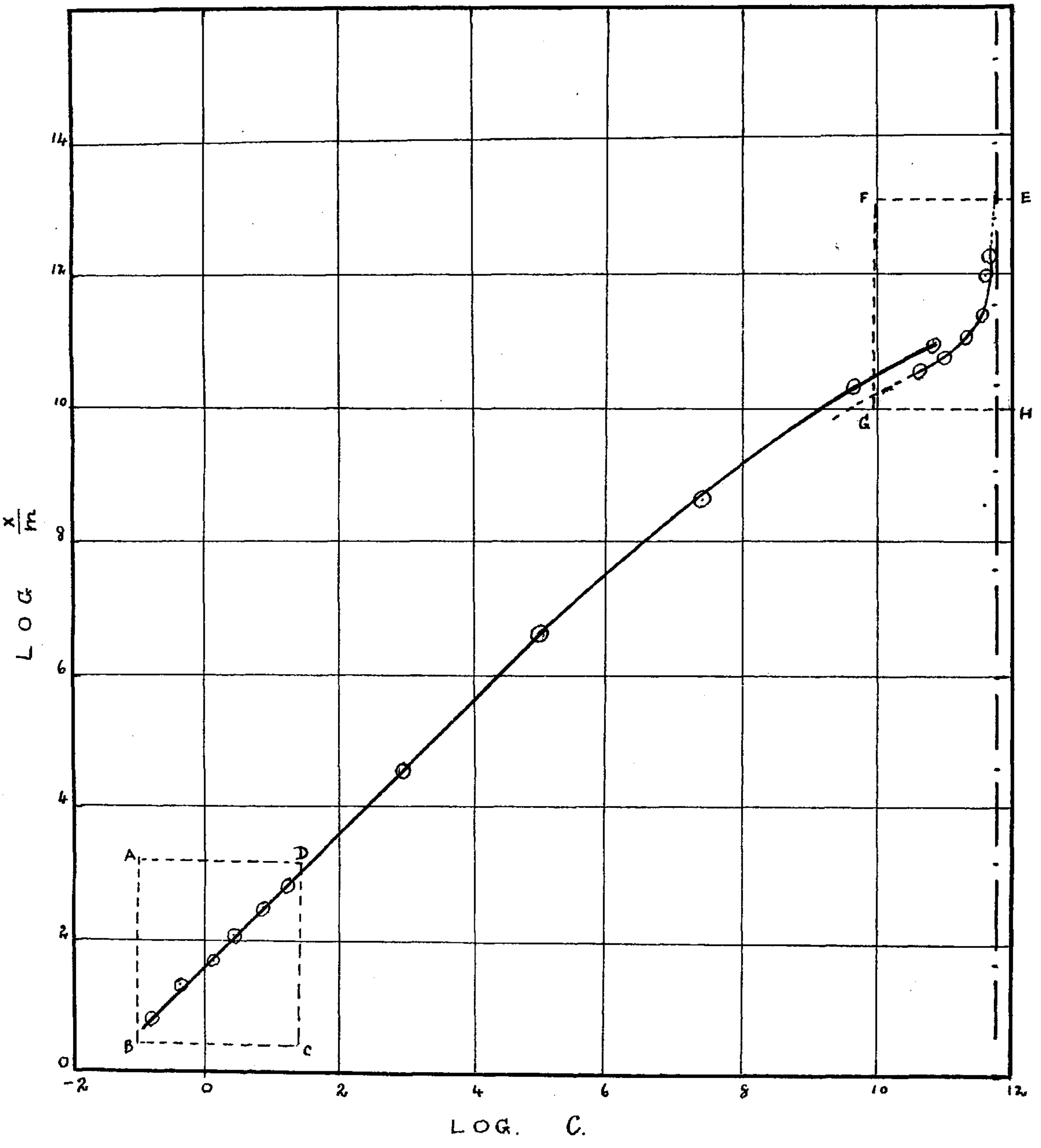
to this reasoning, then $\frac{x}{m}$ can assume any value, while c will remain constant. As a result the graph $\log \frac{x}{m}$, $\log c$, will be a straight line perpendicular to the X axis, and will, in fact, coincide with the solubility limit. The value of $\frac{1}{n}$ for such a graph is infinity.

Returning to a consideration of the experimental evidence, basic ferric acetate, in contact with a saturated solution of basic thorium sulphate (say), adsorbs many layers. These layers, in contact with the nearly saturated solution, will exert a "crystallising action" on the substance still in solution. The nett result is, that the amount of adsorption which takes place is found to be in excess of what one would expect from the course of the graph for more dilute solutions. Considering the case (Exp.6), where the original concentration was a little more than twice the solubility limit, the effect due to crystallisation predominates, masking the geniune adsorption effect. The final result of the two forces at work is shown by the equilibrium concentration being slightly lower than the solubility limit.

When a large excess of thorium nitrate is originally present, (Exp.7), the adsorptive force is completely overshadowed, and the phenomenon may be regarded as a crystallisation, the equilibrium concentration being almost identical with the solubility limit. At this point on the graph it will be observed that the value of $\frac{1}{n}$ rapidly approaches infinity, which is the theoretical value for crystallisation, regarded as an adsorption phenomenon.

In Fig.B, the complete course of the isotherm for the adsorption of uranium X and its isotope thorium by basic ferric acetate, is depicted. A,B,C,D, encloses the part of the isotherm obtained with uranium X alone, and E,F,G,H, is Fig. A on the reduced scale. The two curves illustrating Part 1 and Part 11 while not in exact alignment, are so within the experimental error considering that there was a lapse of one year between the experiments, and considering slight alterations were made to the electroscope in the interval.

FIG. B.



─ · ─ · ─ · ─ = SOLUBILITY LIMIT

Summary.

1. The isotherm for the adsorption of thorium by basic ferric acetate at the point of saturation has been investigated.

2. The value of $\frac{1}{n}$ was observed to pass through a point of inflection, then rapidly increase in value to infinity.

3. Crystallisation, as a special case of adsorption, is discussed, and an interpretation of the experimental observations is offered along these lines.

4. A graph is given, which illustrates the course of the adsorption isotherm of hetratope " atomic number 90" by basic ferric acetate, from infinite dilution, up to the solubility limit.

THE ACTION OF MONOCHLORMETHYLETHER

on

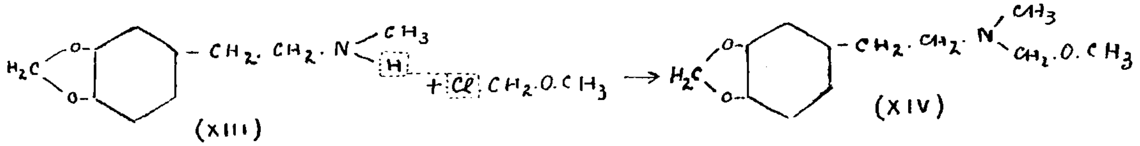
PRIMARY, SECONDARY and TERTIARY AROMATIC AMINES

The Action of Monochlormethylether on Aromatic Amines.

The object of this research was to examine the reactions between monochlormethylether and the primary, secondary and tertiary aromatic amines. In studying the reaction with primary aromatic amines, the action on aniline, p-toluidine and o-nitraniline was examined. The action on secondary aromatic amines was examined for monoethylaniline, while in the case of tertiary aromatic amines, the action on dimethylaniline and diethylaniline was investigated.

Reference to previous work on the action of monochlormethylether on primary and secondary amines is scanty. A patent by E. Merk (D.R.P. 273323 C.1914 1. 1718) describes a process for the preparation of alkyl and aralkyl-amino-methylalkyl ethers, of the general formula alkyl - o - CH_2.N. R' R" (R' = alkyl or Aralkyl, R" = hydrogen or alkyl), by the action of one mol. of a halogen methylalkyl ether (halogen.CH_2O.Alkyl) on two mols. of a primary or secondary amine of the aliphatic, or fatty aromatic series, in an indifferent solvent.

For example, N-Methylmethoxymethylhomopiperonylamine (XlV) is formed by the action of monochlormethylether on N-Methylhomopiperonylamine (Xlll).



The author could find no reference to the action of monochlomethylether on the primary or secondary aromatic amines.

<u>Preparation of Monochlormethylether</u> (Ber. 1907, 40, 4307).

Monochlormethylether is readily formed when dry hydrogen chloride is passed into a cooled mixture of methyl alcohol and paraformaldehyde.

$$CH_3OH + CH_2O + HCl \rightleftharpoons \underset{(1).}{CH_3OCH_2Cl} + H_2O.$$

The equilibrium mixture obtained separates into two layers, the upper of which contains the monochlormethylether (1). Details of the preparation are given on page.........54. Monochlomethylether, B.P. 59-60°C., is a colourless, mobile liquid, it fumes strongly in air and it is very rapidly hydrolised by water, reforming formaldehyde, methyl alcohol and aqueous hydrochloric acid.

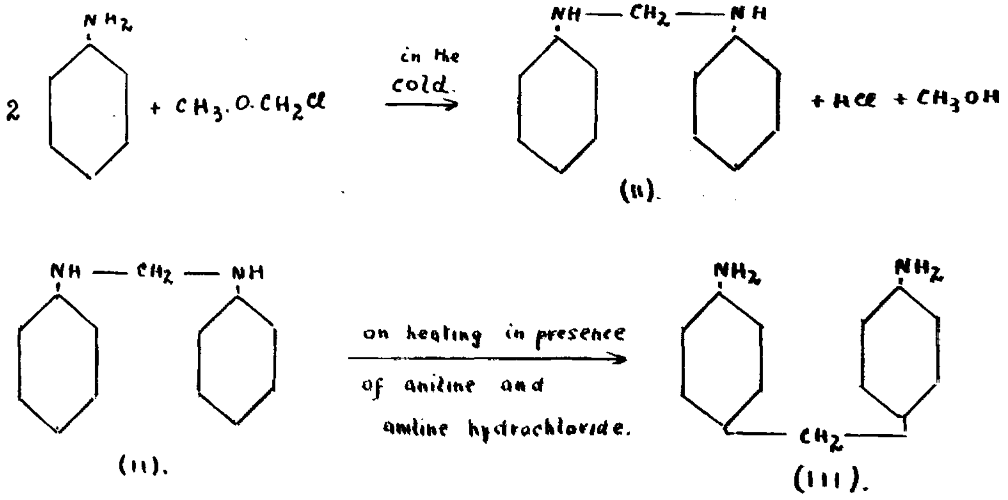
Action of Monochlormethylether on Primary Aromatic Amines.

Action on aniline (in the cold).

One equivalent of monochlormethylether was added to two equivalents of aniline, in presence of excess of dried borax. The reaction was carried out in chloroform, and the temperature was kept below -5 °C. A semi-solid product was obtained which could not be purified for analysis. From its reactions it was believed to contain di-(phenylamino) methane (11).

Action on aniline (in the heat).

On adding monochlormethylether to a large excess of aniline in the cold, and heating the mixture to 150°C. for one hour, 4:4' - diamino-diphenylmethane (111) was formed in good yield. The complete course of the action of monochlormethylether on aniline is probably represented by the following equations.

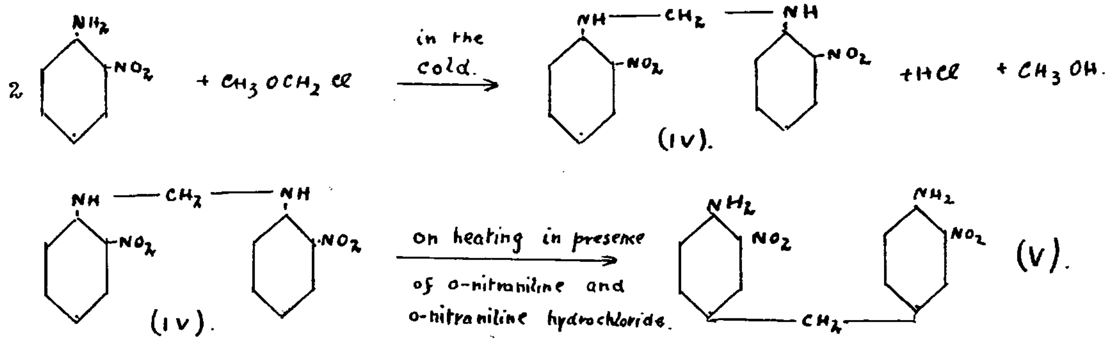


Action on o-nitraniline (in the cold).

A solution of monochlormethylether in dry ethyl ether was added to a solution of o-nitraniline in the same solvent, in the ratio of 1 mol. of the former to 2 mols. of the latter, basic lead carbonate being present to remove the hydrochloric acid as it was formed. Di(2-nitro-phenylamino) methane (IV) was formed in good yield.

Action on o-nitraniline (in the heat).

Monochlormethylether was added to excess of solid o-nitraniline, and the mixture heated to 150°C. for 1 hour. 3:3'-dinitro-4:4'-diamino-diphenylmethane (V) was formed. The course of the reaction is as follows:-



Action on p-toluidine (in the cold)

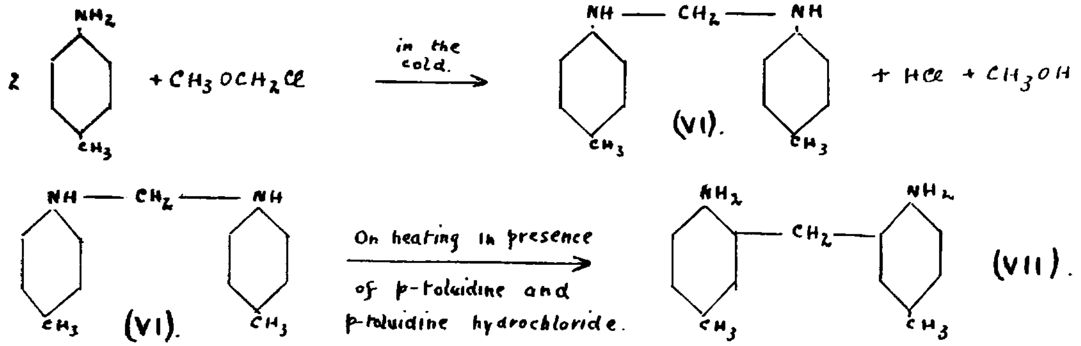
One equivalent of monochlormethylether, dissolved in dry ethyl ether, was added to two equivalents of p-toluidine also dissolved in/

in ether, in presence of excess of basic lead carbonate. The temperature was kept below 5 °C. by means of ice and salt. Di(4-methyl-phenylamino) methane (Vl) was formed almost exclusively.

Action on p-toluidine (in the heat).

Monochlormethylether was added to a large excess of dry p-toluidine and the mixture then heated to 150°C. for 1 hour. 6:6'-diamino-3:3'-dimethyl-diphenylmethane (Vll) was produced.

The complete reaction may be represented by these two equations.



Action of Monochlormethylether on Secondary Aromatic Amines.

Action on monoethylaniline (in the cold.)

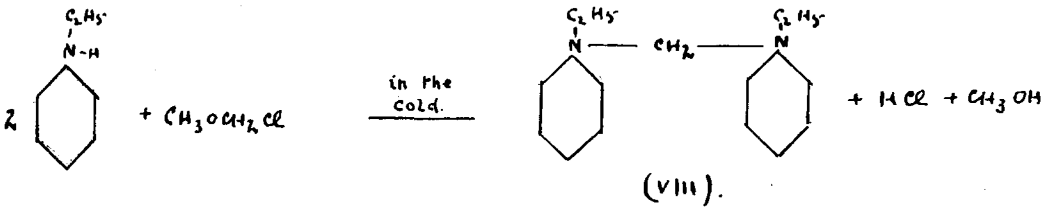
Monochlormethylether, dissolved in dry petroleum ether, was added to two equivalents of monoethylaniline also dissolved in dry petroleum ether, in presence of dried borax. The temperature was/

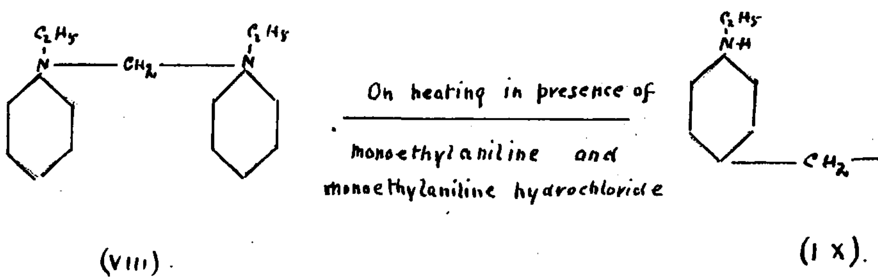
was kept below $5^{\circ}C$. Di(ethylphenylamino) methane (V111) was formed almost quantitatively.

Action on monoethylaniline (in the heat).

Monochlormethylether, dissolved in a neutral solvent (in this case carbon tetrachloride), was added to excess of monoethylaniline also dissolved in carbon tetrachloride, and the mixture then heated under reflux for 30 minutes. Sym. diethyl-4:4'-diamino-diphenylmethane (1X) was formed in good yield.

The pure product was a white crystalline solid, and melted at 17°C. J. v. Braun (loc. cit.), who prepared this compound by another method, records it as an oil. The complete reaction between monochlormethylether and monoethylaniline may be represented thus:-





Discussion of the Reactions between Monochlormethylether and Primary and Secondary Aromatic Amines.

Early in the investigation the similarity of these products, and those produced by the action of formaldehyde and of methylene diiodide on primary aromatic amines, and of formaldehyde on secondary aromatic amines, was evident.
L. Pratesi (Gazzetta 14, 351-356) showed that, when aqueous solutions of aniline and formaldehyde are mixed and allowed to stand, di (phenylamino) methane (11) is formed.

Following up this work, Eberhardt and Welter (Ber. 1894, 27, 1804) showed that similar derivatives of the primary aromatic amines were obtained when two mols. of the base were mixed with one mol. of aqueous formaldehyde, in presence of alcohol and potassium hydroxide, and the mixture boiled for some time.
Meyer and Rohmer (Ber. 1900, 33, 252) prepared di(2-nitrophenylamino) methane (1V) in a similar manner by dissolving o-nitraniline in alcohol and water, and adding aqueous formaldehyde to the boiling mixture.
Senier and Goodwin (J. 1902, 81, 284) found that, in general/

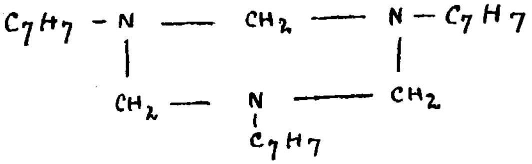
general, when a mixture of one mol. of methylene diiodide and two mols. of a primary aromatic amine and excess of dry potassium carbonate is heated to 150°C., a violent reaction takes place, and the corresponding di(phenylamino) methane derivative is produced.

J. v. Braun (Ber. 1908, 41, 2, 2145) examined the reaction between formaldehyde and secondary aromatic amines in neutral or alkaline solution. He obtained the di(alkylphenylamino) methane derivatives, in a manner entirely analogous to the production of di(phenylamino) methane (11) from aniline and formaldehyde.

Summarising the preceeding references, formaldehyde, in absence of acids, can condense with primary and secondary aromatic amines to form di (phenylamino) methane and di (alkylphenylamino) methane derivatives.

These di (phenylamino) methane and di (alkylphenylamino) methane compounds, while stable when pure, are very reactive and yield a variety of products. For example, di(4-Methyl-phenylamino) methane (Vl), the p-toluidine derivative, on heating, forms free p-toluidine and an insoluble amorphous/

amorphous product of uncertain structure. Again, on boiling with alcohol or water, the major portion is resolved into p-toluidine and formaldehyde, while small quantities of other more stable compounds of p-toluidine and formaldehyde are formed. One of these, anhydroformaldehyde-p-toluidine (x), M.P. 127-128°C., has been ascribed this formula (Bischoff Ber. 1898, 31, 3253):-



(x).

Bischoff deduces this from molecular weight determinations in boiling benzene, and also from the fact that it is a tertiary amine.

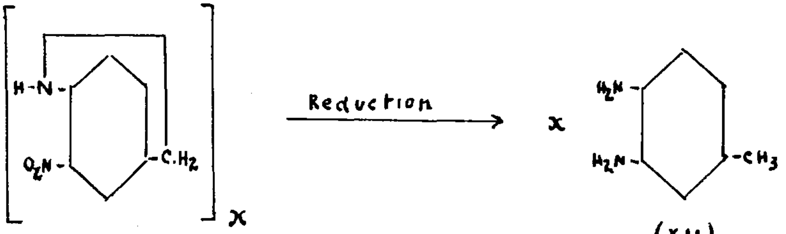
On treatment with hydrochloric acid, profound alteration in the structure of these di(phenylamino) methane and di (alkylphenylamino) methane compounds may result; polymers of anhydroaminobenzyl alcohol may be formed, together with liberation of the original base.
On more vigorous treatment with hydrochloric acid, diphenylmethane derivatives are formed. Meyer and Rohmer (loc. cit.) treated di (2-nitro-phenylamino) methane (1V) with concentrated hydrochloric acid in the cold, and obtained/

obtained an amorphous body ($(C_7H_6N_2O_2)_x$ (Xl) and o-nitraniline. On heating, they obtained finally, 3:3'-dinitro-4:4'-diamino-diphenylmethane (V). They postulate the reaction thus,

$$\underset{(IV)}{CH_2(NH.C_6H_4.NO_2)_2} \xrightarrow[\text{cold.}]{HCl} NH_2.C_6H_4.NO_2 + \underset{(XI).}{(C_7H_6N_2O_2)_x}$$

$$NH_2.C_6H_4.NO_2 + (C_7H_6N_2O_2)_x \xrightarrow{\text{on heating}} CH_2(C_6H_3NH_2.NO_2)_2 \quad (V).$$

They examined the intermediate amorphous substance. On vigorous reduction with zinc and hydrochloric acid it yielded 3:4 -diamino-toluene (Xll), which is strong evidence that the highly polymerised substance contained the p.-anhydroaminobenzyl alcohol linkage.



(XI) (XII).

By condensing primary aromatic amines and formaldehyde in dilute mineral acid, P.M. Kroneburg (J. Russ, Phys, Chem. Soc., 1916, 48, 305-309) obtained similar amorphous substances. The melting point of the product varied with the temperature at which the reaction was carried out. Molecular weight/

weight determinations, in freezing nitrobenzene, gave values of over 1,000. The compounds were believed to contain the ortho-or para-anhydroaminobenzyl alcohol linkage.

By boiling the di(alkylphenylamino) methane derivatives of the secondary aromatic amines with concentrated hydrochloric acid for 10 hours, J.v. Braun (Loc. cit.) obtained the corresponding diphenylmethane derivatives; v. Braun remarks, that when the ortho or para position is occupied, the quantity of higher condensation products formed is considerably reduced.

Eberhardt and Welter (loc. cit.) bring about the intramolecular change of the di (phenylamino) methane derivatives obtained from the primary aromatic amines, into the isomeric diphenylmethane derivatives, by heating for 10 hours with the hydrochloride of the original base and some free base. The course of the transformation is not clear, it may be that the anhydroaminobenzyl alcohol linkage is momentarily formed.

Turning now to a consideration of the reaction of monochlormethylether on primary and secondary aromatic amines, the isolation of the di (phenylamino) methane and di (alkyl-phenylamino) methane derivatives is conditional on/

on the rapid removal of the liberated hydrochloric acid. That this removal is not sufficiently rapid, may account for the inability to isolate di (phenylamino) methane (11), which is the most reactive of the series.

When monochlormethylether is added to excess of the base, it is obvious that we have present the identical mixture which Eberhardt and Welter (loc. cit.) heated, in order to bring about the formation of the diphenylmethane derivatives. On heating the mixture the same products are obtained.

It is of interest to observe that, while the aliphatic primary and secondary amines form N-methoxymethyl compounds with monochlormethylether (E. Merk loc. cit.), no such derivatives of the aromatic amines were observed. It is possible that such compounds are momentarily formed, and immediately react with a further molecule of the base.

If such is the case, the formation of the di(phenylamino) methane and di(alkylphenylamino) methane derivatives of the primary and secondary amines would be represented by these two equations:-

$$R'R''.N-H \quad + \quad ClCH_2OCH_3 \longrightarrow R'R''.N-CH_2OCH_3 \quad + HCl$$

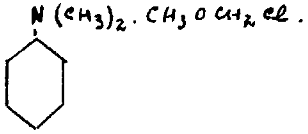
$$R'R''.N-CH_2OCH_3 \quad + \quad H-N.R''R' \longrightarrow R'R''.N-CH_2-N.R''R' \quad + CH_3OH$$

(R' = aryl , R'' = alkyl or hydrogen).

Action of Monochlormethylether on Tertiary Aromatic Amines.

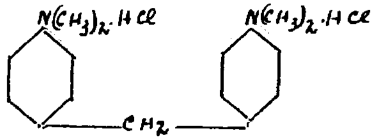
Action on Dimethylaniline.

Dunlop (J. 1914, 105, 1156) attempted to form the quaternary ammonium compound (XV) between monochlormethylether and dimethylaniline,



(XV),

with the view of obtaining a compound to characterise monochlormethylether. He, however, obtained the hydrochloride of tetramethyl - 4:4' - diamino-diphenylmethane (XVI).

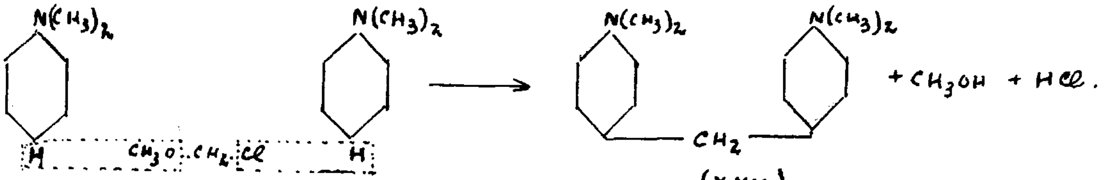


(XVI).

No details of the experimental work are given.

It was found that, on adding one mol. of monochlormethylether to two mols. of dimethylaniline dissolved in carbon tetrachloride and refluxing the mixture for several hours, an almost quantitative yield of tetramethyl - 4:4'-diamino-diphenylmethane (XVII) was/

was formed. The reaction may be represented thus:-



(XVII).

In order if possible to trace the course of the reaction,a series of experiments were conducted at 0°C. Equimolecular quantities of dimethylaniline and monochlormethylether,in petroleum ether solution at -10°C.,were mixed. No apparent reaction took place. On standing several hours in the ice-chest, a white precipitate appeared. On examination, this substance proved to be a mixture of dimethylaniline hydrochloride and the quaternary ammonium compound of di methylaniline and monochlormethylether (XV). The filtrate contained free dimethylahiline, tetramethyl--4:4'-diamino-diphenylmethane (XVII), and unchanged monochlormethylether. The smell of methylal was observed.

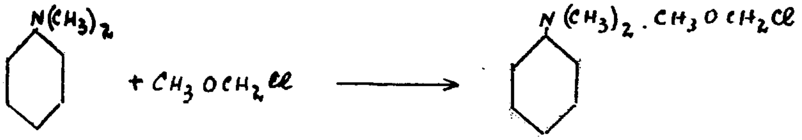
As the reaction in the above experiment was obviously not completed, a similar experiment was carried out and this time two weeks were allowed for the reaction to proceed. The solid obtained from this experiment was found to be a mixture of tetra methyl-4:4'-diamino-diphenylmethane hydrochloride (XVI) in admixture with the di-quaternary ammonium compound of that substance (XVIII). Traces of dimethylaniline hydrochloride and the quaternary /

quaternary ammonium compound of dimethylaniline were also present. The filtrate contained only a trace of tetramethyl-4:4'-diamino-diphenylmethane (XV11). As the solid mixtures obtained in these two experiments were very hygroscopic, no attempt was made to separate them into their components. Some of the di-quaternary ammonium compound of tetramethyl-4:4' - diamino-diphenylmethane (XV111) was, however, prepared by mixing equivalent quantities of monochlormethylether and tetramethyl-4:4'-diaminodiphenylmethane (XV11) in petroleum ether, and allowing the mixture to remain at room temperature for a fortnight.

The evidence indicating the presence of the quaternary ammonium compounds is given in the experimental section.

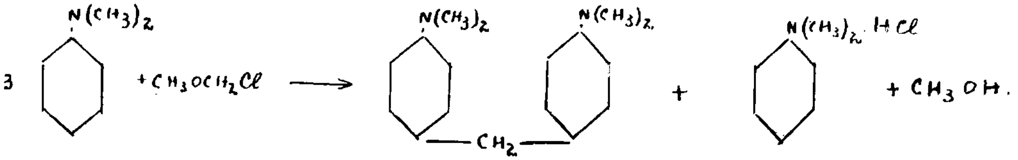
The general course of the reaction between equimolecular quantities of dimethylaniline and monochlormethylether in the cold, may be represented by the following three equations, each reaction taking place with comparative slowness.

I.



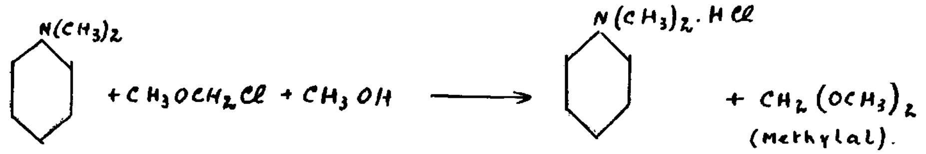
(XV).

II.

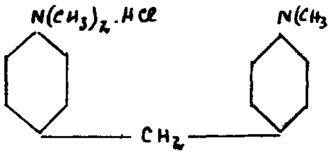


(XVII).

III.

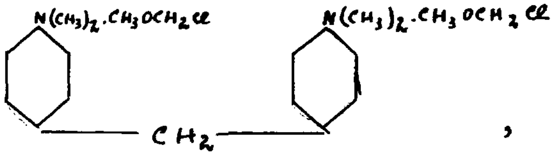


on continued standing, we get finally, as the main products of the reaction, a mixture of tetramethyl - 4:4'-diamino-diphenylmethane hydrochloride (XVl) and the di-quaternary ammonium compound of that base with monochlormethylether (XV111),



(XVI).

and



(XVIII).

,

together with small quantities of dimethylaniline hydrochloride, methylal and methylalcohol.

Action on Diethylaniline.

Diethylaniline reacts similarly to dimethylaniline on treatment with monochlormethylether in a neutral solvent/

solvent, and heating the mixture. Tetraethyl - 4:4'-diaminodiphenylmethane is formed. The reaction, however, proceeds more slowly.

Experimental.

Preparation of Monochlormethylether (Ber. 1907, 40, 4307)

210 grams of paraformaldehyde and 224 grams of methylalcohol are placed in a two-litre flask, immersed in a freezing mixture, and a rapid stream of dry hydrogen chloride passed in. The paraformaldehyde gradually disappears, and the mixture separates into two layers. The upper layer, which contains the monochlormethylether, is separated from the lower layer and dried over anhydrous calcium chloride, it is then distilled through a fractionating column. The fraction which distils between 58·5 - 60°C. is collected.

Yield = 330 grams.

The pure product was preserved in a stoppered bottle, some dried powdered borax being added to absorb any dissolved hydrogen chloride.

Attempts to distil the crude product without previous drying over calcium chloride were unsuccessful, large volumes of hydrogen chloride were given off, and a low boiling liquid, identified as methylal, distilled over. This decomposition was due to the presence of free methyl alcohol which reacts with monochlormethylether thus:-

$$CH_3OCH_2Cl + CH_3OH \longrightarrow CH_2(OCH_3)_2 + HCl.$$

By treating the crude product with calcium chloride the free methyl alcohol is removed.

Analysis of Monochlormethylether.

A weighed quantity was mixed with a large volume of cold distilled water. Hydrolysis was complete in a few seconds.

$$CH_3OCH_2Cl + H_2O \longrightarrow CH_3OH + CH_2O + HCl$$

The hydrochloric acid formed was then titrated with N/10 sodium hydroxide, using phenolphthalein as indicator.

0·3095 gram on hydrolysis formed ·1398 gram HCl.

theoretically there should be formed ·1403 " "

The monochlormethylether was therefore assumed to be pure.

The Action of Monochlormethylether on Primary Aromatic Amines.

Action on Aniline (in the cold).

28 grams of pure aniline (2 mols), dissolved in 100 c.c. of chloroform, were placed in a bottle fitted with a stirrer. 20 grams of borax, previously dried at 160°C. for several/

several hours were then added and the mixture cooled to -10°C. 12·7 grams of monochlormethylether (1 mol), in 50 c.c. of chloroform were now slowly run in. The temperature was kept below -5°C. by external cooling. When half of the monochlormethylether solution had been added, the addition was discontinued for about two hours to permit any aniline hydrochloride present to be converted into the free base by the borax. The addition was then continued till three quarters had been added, and again stopped. Finally, the last quarter of the monochlormethylether solution was slowly added. Stirring was continued for a further hour.

The chloroform solution was filtered, the residue washed with a little chloroform, and the combined chlorform solutions evaporated under reduced pressure at room temperature. The product was a pale yellow viscous oil, weighing 22 grams. On adding a few c.c. of ether, the mass became opaque and, on standing, semi-solid.

This semi-solid mass was too unstable to purify, but it resembled di (phenylamino) methane (11) in its properties. It was easily soluble in alcohol, and on boiling the solution, anhydroformaldehyde aniline (M.P. 140°C) was deposited, along with a high melting amorphous body. In this respect/

respect it resembles the product obtained by Pratesi (loc. cit.), and by Eberhardt and Welter (loc. cit.). That di-(phenylamino) methane is difficult to isolate, is emphasised by Senier and Goodwin.

The residue of sodium chloride and excess borax was dissolved in water; about two grams of a substance, M.P. 205-220°C, insoluble in alcohol, ether and chloroform, was obtained. This was not examined further.

Action on Aniline (in the heat)

Several preliminary experiments were carried out using carbon tetrachloride as solvent. The reaction between aniline and the monochlormethylether, however, was very rapid, and the solid hydrochloride, which separated, made mixing difficult.

By using excess of aniline as the solvent, the reaction proceeded smoothly and, by regulating the temperature, separation of solids could be avoided. 17·3 grams of Monochlormethylether (1 Mol.) were run slowly into 80 grams of pure dry aniline (2 mols.) at 20°C, with rapid stirring. The temperature rose rapidly, and was kept just below 30°C. When the addition was complete, the temperature was raised to 100°C, the flask being fitted with a reflux condenser. As a liquid appeared to be slowly refluxing, the condenser was/

was arranged as for distillation, when about 5 c.c. of a liquid passed over. This was subsequently identified as methylalcohol.

The temperature of the mixture was now raised to 150°C. for one hour. When cold, excess of ammonium carbonate solution was added, and the mixture steam-distilled till all trace of aniline was removed. An oil was left in the flask which, on standing overnight, became semi- solid, while flaky crystals had appeared in the supernatant aqueous layer.

Weight of product 40·1 grams.

The flaky crystals, on recrystallisation from carbon tetrachloride, melted at 91°C., corresponding to 4:4'-diamino-diphenylmethane (111) Attempts to recrystallise the main bulk of product were unsatisfactory, it was purified by distillation in vacuo. The fraction which came over between 248-251°C at 16 m.m. was collected, it solidified to a pale yellow solid on cooling. 25·2 grams distilled over.

This substance, on recrystallisation from carbon tetrachloride, melted at 91°C., corresponding to 4:4'-diamino-diphenylmethane.

N found = 14·21%
Theory requires 14·14%

A little of the product on ethylation with excess of ethyl iodide, and a still greater excess of aqueous sodium carbonate, yielded a product which, on re- /

recrystallisation from methyl alcohol, melted at 42°C., corresponding to sym-tetraëthyl - 4:4'-diamino-diphenylmethane. A mixed melting point with the latter substance produced no depression.

Action on O-Nitraniline (in the cold).

A mixture of 25·4 grams of o-nitraniline (2 mols.) in 150c.c. ethyl ether, and 16 grams of basic lead carbonate, was agitated in a bottle at room temperature. 7·5 grams of monochlormethylether (1 mol) in 40 c.c. of ethyl ether were then slowly added . The time of addition was 45 minutes and the temperature rose from 14·5°C. to 21°C. Stirring was continued for a further hour. The ethereal layer contained chiefly free o-nitraniline, the main yield being mixed with the lead salts. The ether was evaporated under reduced pressure and the combined solids were then extracted several times with boiling alcohol. Yellow crystals were obtained on cooling the hot alcoholic solutions which, on recrystallisation from alcohol, melted at 193°C. The yield of the pure product was 7 grams.

This corresponds to di (2-nitro-phenylamino) methane (lV), M.P. 195°C., obtained by Meyer and Rohmer. A little of this substance was prepared by their method, previously described. A mixed melting point with the above substance showed/

showed no depression.

Action on O-Nitraniline (In the heat).

10 grams of monochlormethylether were added to 51 grams of o-nitraniline, and the solid mixture heated directly to 150°C. in an oil bath for 1 hour. A low boiling liquid refluxed which smelt of methylal; fumes of hydrochloric acid were also given off. The mass in the flask finally became semi-liquid. When cold, the contents of the flask were boiled with excess of sodium carbonate solution and the residue filtered off. When dry, it was extracted with hot alcohol, when 25 grams of a product, insoluble in alcohol, were obtained. This substance, on recrystallisation from acetone, yielded brick red crystals, M.P. 222-224°C., which corresponds to 3:3'-dinitro-4:4'-diamino-diphenylmethane, of M.P. 224°C., obtained by Meyer and Rohmer.

N found	= 19·40%
Theory requires	19·44%

Action on p-toluidine (in the cold)

18·1 grams of pure p-toluidine (2 mols.), dissolved in 80 c.c. of ethyl ether, were/

were placed in a bottle fitted with a stirrer, 30 grams of basic lead carbonate (excess) were added, and the mixture cooled to 0°C. 6·9 grams of monochlormethyl ether (1mol.), contained in 40 c.c. of ethylether, were now alowly added during half-an-hour. The maximum temperature recorded during the addition was 5°C. After stirring a further hour the ethereal solution was filtered, and evaporated under reduced pressure at room temperature. A solid residue was left, weighing 16 grams. This residue was washed with 30 c.c. of cold alcohol, when 7·8 grams of a very pale yellow crystalline solid were obtained, melting at 85-86°C. Recrystallisation from hot alcohol produced slight decomposition; from cold alcohol by spontaneous evaporation, however, the pure product so obtained melted at 87-88°C. This corresponds to di (4 methyl-phenylamino) methane (V1), previously observed to melt at 86°C. — Eberhardt and Welter (loc. cit) and at 89°C. — Eibner (Annalen 1898, 302, 350)

N. found = 12·32%
Theory requires 12·40%

3 grams of this substance were boiled with water in an open flask. The substance melted, and a smell of p-toluidine and formaldehyde was observed. On continued boiling, fine needle-shaped crystals appeared in place of the oil, weighing 0·9 gram. On recrystallisation from/

from acetone two products were obtained, a white amorphous insoluble substance of high melting point, and very long needle-shaped white crystals M.P. 127-128°C. Eberhardt and Welter, in their paper, record a similar reaction when di(4-methyl-phenylamino) methane is boiled for a long time with alcohol, similar products being obtained. The compound M.P. 127-128°C. is anhydroformaldehyde - p - toluidine.

Action on p-toluidine (in the heat).

8·1 grams of monochlormethylether (1 mol.) were added directly to 42 grams of pure dry p-toluidine (4 mols.), and the mixture heated to 150°C. for 1 hour. The odour of methylal was detected.

The product was now rendered alkaline with ammonium carbonate solution, and steam-distilled till all trace of p-toluidine was removed. The product, a non-volatile reddish oil, was purified by distillation in vacuo. The fraction which distilled between 240-250°C. at 25m.m. pressure was collected. 10 grams passed over, and, on standing, it became solid. It was recrystallised from petroleum when short needles were obtained, melting at 94-95°C. This agrees with 6:6'-diamino-3:3'-dimethyl-diphenylmethane (Vll), previously observed to melt at 92°C by Eberhardt and Welter (loc. cit.).

N found = 12·29%
Theory Requires 12·40%

Action of Monochlormethylether on Secondary Aromatic Amines.

Action on Monoethylaniline (in the cold).

The reaction was carried out inasimilar manner to that employed with primary aromatic amines. By the use of basic lead carbonate to remove the liberated hydrochloric acid the product obtained was an oil which could not be purified. Substituting borax, previously dehydrated at 160°C. for several hours, however, in place of basic lead carbonate, a crystalline compound was obtained. After several experiments, it was found best to use a slight excess of monochlormethylether.

41 grams of monoethylaniline, contained in 80 c.c. of petroleum ether (previously dried over sodium), were placed in a bottle fitted with an agitator, 24 grams of dried borax were then added and the mixture cooled to -10°C. 16·2 grams of monochlormethylether in 30 c.c. of petroleum ether were then slowly run in. This operation took 30 minutes and the maximum temperature attained was 5°C. Stirring was continued for a further hour. 50 c.c. of cold water were now added, the mixture stirred, and then transferred to a large/

large bottle and shaken up with one litre of water. The petroleum ether layer was now separated and evaporated in a basin in the open air. The rapid fall of temperature caused tufted needle-shaped crystals to separate, weighing 5 grams, and melting at 70-74°C. The mother liquor became solid on further evaporation. Weight of solid 30 grams. On further recrystallisation from petroleum ether the product was obtained pure, and melted at 77°C.

N found = 11.00%

Theory Requires 11·02%

This corresponds to di(ethylphenylamino) methane (V111), M.P. 76-77°C., obtained by J. v. Braun (loc. cit.).

Action on Monoethylaniline (in the heat).

9·1 grams of monochlormethylether (1 mol.), dissolved in 20 c.c. of carbon tetrachloride, were slowly added to 57 grams of monoethylaniline (4 mols.) in 50 c.c. of carbon tetrachloride cooled to -5°C. The temperature rose to 37°C. and the solution remained clear. The mixture was now boiled under reflux for 30 minutes. The reaction being now assumed to be complete, the fluid was steam-distilled, then rendered alkaline with sodium carbonate, and again steam-distilled till all trace of monoethylaniline was volatilised. A non-volatile reddish oil was left in the flask/

flask, weighing 25·8 grams. The oil did not crystallise and, as it formed a nitroso-deriviative, it was decided to purify it by this means.

Formation of nitroso derivative.

The oil was dissolved in 40 c.c. of concentrated hydrochloric acid in 200 c.c. of water, cooled in ice, and 12 grams of sodium nitrite in 20 c.c. of water slowly added with stirring. The nitroso derivative appeared as an oil, which became semi-solid on standing. 300 c.c. of ether were now added and the mixture shaken up. Only part of the nitroso derivative dissolved, the undissolved portion, however, had become solid. This was filtered off and dried. Weight 16 grams. M.P. 79-80°C. The ethereal layer yielded 4·5 grams of the pure nitroso derivative, as tufted needles, melting at 81°C. This corresponds to the dinitroso derivative of sym. diethyl-4:4'-diamino-diphenylmethane, M.P. 83°C., obtained by J.v. Braun (loc. cit.).

Reduction of the nitroso deriviative.

15·5 grams of the nitroso derivative, 80 grams of stannous chloride and 200 c.c. of concentrated hydrochloric acid, contained in a large beaker, were heated to 40°C. Reduction proceeded smoothly, and on cooling, the tin double/

double salt crystallised out. This was filtered off, decomposed with excess of sodium hydroxide, and the base extracted with ether. 11·3 grams of a pale yellow oil were obtained. As the product did not crystallise, it was further purified by vacuum distillation.

B.P. 260°C. at 20 m.m. pressure.
243°C " 10 m.m. "

The product, a pale yellow viscous oil, was cooled in a mixture of hydrated calcum chloride and ice for several hours, with occasional scratching. The mass gradually solidified. It melted at 17°C.

As sym.diethyl-4:4'-diamino-diphenylmethane (lX) is given as a liquid (J. v. Braun), the constitution of this solid was examined.

Examination of product M.P. 17°C.

Molecular weight determination in freezing benzene gave an average value of 246. Ethylation, by boiling with ethyl iodide and sodium carbonate solution, yielded a product which, on recrystallisation from methyl alcohol, melted at 42°C. A mixed melting point of this substance with tetraethyl - 4:4' diamino-diphenylmethane (M.P. 41°C.) gave a melting point of 41-42°C., proving the substances to be identical.
It was concluded that the substance, M.P. 17°C, was sym. diethyl-4:4'-diamino-diphenylmethane (lX).

Action of Monochlormethylether on Tertiary Aromatic Amines.

Action on Dimethylaniline.

Experiment 1.

10·7 grams of monochlormethylether (1 mol.), dissolved in 40 c.c. of dry carbon tetrachloride, were run slowly into a solution of 32·6 grams of pure dry dimethylaniline (2 mols.) in 60 c.c. of the same solvent, cooled to -10°C. No apparent reaction took place, and the temperature rose only a few degrees. The solution was slowly warmed up, and boiled under reflux for 3 hours; an oily layer appeared on top of the liquid which became solid as the reaction proceeded.

The contents of the flask were steam-distilled to recover the carbon tetrachloride, then rendered alkaline with sodium carbonate, and again steam-distilled till all trace of dimethylaniline was removed. The reddish non-volatile oil became solid on cooling.

Weight 35·5 grams.

On recrystallisation from methyl alcohol, tetramethyl - 4:4'-diamino-diphenylmethane (XVll) was obtained/

obtained pure in the form of glistening plates, which melted at 89°C.

N found = 10·95%
Theory Requires 11·03%

Molecular weight in boiling benzene = 246 (constant used = 50)
Molecular weight calculated = 254.

The yield was practically theoretical and no by-products were observed.

In order, if possible, to trace the course of the reaction, experiments were carried out in the cold.

Experiment 11.

10·65 grams of monochlormethylether (1 mol.) in 20 c.c. of dry petroleum ether, were added to 16·0 grams of dimethylaniline dissolved in 50 c.c. of the same solvent cooled to - 10°C. Only a slight rise in temperature took place, and on standing some time, a very slight only precipitate began to appear. At first this oilyness was thought to be due to moisture, but it was finally attributed to the formation of methyl alcohol. On standing overnight in the ice-chest, a white bulky precipitate had appeared. This was filtered off, washed with petroleum ether, and dried over sulphuric acid in a desiccator. This substance was very hygroscopic, and sublimed on to the sides of the desiccator.

It/

It smelt strongly of formaldehyde.

Weight 16·4 grams. M.P. 60-64°C.

The filtrate, on evaporation,was found to contain unchanged dimethylaniline, some monochlormethylether, together with some tetramethyl - 4:4' - diamino-diphenylmethane (XV11). The presence of methylal was observed.

Experiment 111.

Obviously the reaction in Exp. 11, was incomplete, it was repeated,and this time left for a fortnight in the ice-chest. The solid was as before filtered off, washed,and preserved in a desiccator, The filtrate contained only a trace of tetramethyl - 4:4' -diamino-diphenylmethane.

Examination of the products from experiments 11, and 111.

5 grams of the product from exp. 11, were dissolved in cold water and excess of sodium hydroxide solution rapidly added. The mixture was now turbid and was extracted with ether, leaving a clear alkaline solution. The ether extract,on examination,contained 2·4 grams of dimethylaniline and a trace of tetramethyl - 4:4' - diamino-diphenylmethane.

The clear alkaline solution gradually became turbid, and after standing overnight,it was again extracted with ether. This ether extract,on examination,was also found to contain dimethylaniline and a trace of tetramethyl - 4!4'-diamino-diphenylmethane.

From the above observations it was thought that the product from exp. 11, was a mixture of dimethylaniline hydrochloride and the quaternary ammonium compound of dimethylaniline and monochlormethylether (XV), and that on adding excess of sodium hydroxide to the solution of this product, free dimethylaniline was liberated from the one constituent, while the other formed an unstable quaternary ammonium hydroxide compound which remained in solution. On standing, however, this compound became hydrolysed with formation of free dimethylaniline, formaldehyde and methyl alcohol; the gradually developing turbidity, after the first extraction with ether, being due to the dimethylaniline thus slowly formed.

If this hypothesis is correct, we would expect a lag in the end-point when some of the product from exp. 11, is titrated with sodium hydroxide solution, using an indicator.

0·225 gram of the product from exp. 11 was dissolved in cold water and titrated with N/10 sodium hydroxide, using phenolphthalein as indicator. 11·3 c.c. were required. The solution was now warmed, when it again assumed an acid reaction. The end-point was followed up till finally the boiling solution required altogether 14·6 c.c. of N/10 sodium hydroxide.

This confirmed the view that the product from exp. 11,

was/

was a mixture of dimethylaniline hydrochloride and the quaternary ammonium compound of dimethylaniline and monochlormethylether, together with traces of tetramethyl - 4:4'-diamino-diphenylmethane hydrochloride and the diquaternary ammonium compound of that substance and monochlormethylether.

Examination of the product from Exp. 111, on the same lines, gave slightly different results.

5 grams in water, on being made alkaline, gave a solid precipitate of tetramethyl -4:4'-diamino-diphenylmethane, while the filtrate, on standing, slowly deposited a further crop of crystals of the same substance.

A titration experiment on the same lines as before again showed a lagging endpoint.

From these tests, it was concluded that the product from Exp. 111 was a mixture of tetramethyl-4:4'-diamino-diphenylmethane hydrochloride (XV1), and the di-quaternary ammonium compound of that base and monochlormethylether (XV111). Traces of dimethylaniline hydrochloride and the quaternary ammonium compound of dimethylaniline and monochlomethylether were also present.

Preparation of the di-quaternary ammonium compound of tetra-methyl-4:4'-diamino-diphenylmethane and monochlormethylether.

1·6 grams of monochlormethylether were added to 2 grams of tetramethyl - 4:4'-diamino-diphenylmethane dissolved in 30 c.c. of warm petroleum ether, and the flask tightly stoppered. No apparent reaction took place, but on standing overnight, a precipitate had begun to appear. The reaction was allowed to proceed for a fortnight, when the di-quaternary ammonium salt was filtered off. It was noticed that the precipitate was bluish green where it had been exposed to light. The solid was hygroscopic, and was preserved in a desiccator over sulphuric acid.

Analysis of Product.

0·712 gram was dissolved in cold water and titrated with N/10 sodium hydroxide using phenolphthalein as indicator, the end-point was rather indefinite; 17·9 c.c. of N/10 sodium hydroxide were required. On warming, an acid reaction developed, and the end-point was followed up. Finally 34·55 c.c. N/10 sodium hydroxide were required, corresponding to an equivalent of 206. The di-quaternary ammonium compound requires an equivalent of 208·5.

Tetramethyl - 4:4'-diamino-diphenylmethane was liberated unchanged.

Action on Diethylaniline.

15·6 grams of monochlormethylether, in 40 c.c. of carbon tetrachloride, were added to 72·3 grams of pure redistilled diethylaniline contained in 60 c.c. of the same solvent, cooled to -10°C. No apparent reaction took place. The mixture was boiled under reflux for two hours, when a dark oily layer appeared on top. Excess of dilute hydrochloric acid was now added, and the mixture steam-distilled to remove the carbon tetrachloride. Some formaldehyde also distilled over indicating that the reaction was not completed. The mixture was now rendered alkaline, and steam-distilled. The non-volatile oil left in the flask did not crystallise, it was taken up in ether and dried over sodium sulphate. On concentration, crystals appeared. These were recrystallised from methyl alcohol, when 10·5 grams of the pure product melting at 41°C., were obtained. This corresponds to tetraethyl - 4:4'-diamino-diphenylmethane.

N found = 9·10%
Theory Requires 9·03%

Summary.

1. The action of monochlormethylether on primary, secondary and tertiary aromatic amines has been investigated.

2. The reaction with primary and secondary aromatic amines proceeds in two stages.
    1. When the reaction is carried out in the cold, the primary aromatic amines form di(phenylamino) methane derivatives while the secondary aromatic amines form di(alkylphenylamino) methane derivatives.
    2. When the temperature of the mass is raised, intramolecular change occurs, and the corresponding diphenylmethane derivatives are produced; the linkage takes place in the para position to the animo group, or in the ortho position when the former is occupied.

3. The tertiary aromatic amines react slowly in the cold and more rapidly when the temperature is raised. In each case the diphenylmethane derivative is formed. When the reaction is carried out in the cold, the presence of quaternary ammonium compounds of monochlormethylether and the original base, and also of the resultant diphenylmethane derivative, has been proved.

LIST OF ABBREVIATIONS.

Abbreviated Title.	Journal.
Annalen.	Justus Liebig's Annalen der Chemie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
C.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'académie des Sciences.
D.R.-P.	Deutsches Reichs-Patent.
Gazzetta.	Gazzetta chimica italiana.
J.	Journal of the Chemical Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Russ. Phys. Chem.Soc.	Journal of the Physical and Chemical Society of Russia.
Medd. K-Vet.Nobelinstitut.	Meddelanden från Kough-Vetensk: apsakademiens Nobel-Institut.
Monatsh.	Monatshefte für Chemie und verwandte Tiel anderer Wissenschaften.
Physikal Zeitsch.	Physikalische Zeitschrift.
Z.physikal Chem.	Zeitschrift für physikalische Chemie, Stochiometric und Verwandschaftslehre.
