

304. *Infusible White Precipitate: Some New Evidence as to its Structure, from a Study of its Thermal Decomposition.*

By D. R. GLASSON and S. J. GREGG.

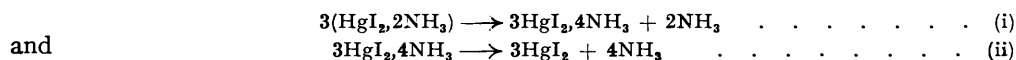
Measurements have been made of (a) the rate of thermal decomposition, (b) the total loss in weight (due to evolution of ammonia), and (c) the dissociation pressure, on the compounds $\text{HgCl}_2 \cdot 2\text{NH}_3$, $\text{HgI}_2 \cdot 2\text{NH}_3$, and $3\text{HgI}_2 \cdot 4\text{NH}_3$; and of (a) and (b) on $\text{HgCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ and infusible white precipitate. From (a) the energy of activation E , and from (c) the heat of dissociation $-\Delta H$, have been calculated for the loss of ammonia (or of pyridine) from the compounds. Comparison of the value of E for infusible white precipitate with the values of E and of $-\Delta H$ for the other compounds shows that Britton and Wilson's formula $\text{HgO} \cdot \text{HgCl}_2 \cdot 2\text{NH}_3$ is more probable than the customary Franklin formula $\text{NH}_2 \cdot \text{HgCl}$ or the older Rammelsberg formula $\text{NH}_2\text{Hg}_2\text{Cl} \cdot \text{NH}_4\text{Cl}$. This conclusion is supported by the data under (b) and also by the fact that the content of "basic" mercury (HgO) in infusible white precipitate is unaltered by heating.

The formation of the complex $\text{HgCl}_2 \cdot 0.67\text{NH}_3$ in the dry way does not appear to have been reported before.

THE structure now usually assigned to infusible white precipitate is $\text{NH}_2 \cdot \text{HgCl}$ (I) (Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35; Partington, "General and Inorganic Chemistry," 1949, p. 402), rather than the earlier formula $\text{NH}_2\text{Hg}_2\text{Cl} \cdot \text{NH}_4\text{Cl}$ (II) (Rammelsberg, *J. pr. Chem.*, 1883, **38**, 558; Pecci, *Gazzetta*, 1889, **19**, 509; 1890, **20**, 485; *Z. anorg. Chem.*, 1899, **21**, 362). Britton and Wilson (*J.*, 1932, 2550; 1933, 601, 1043), however, have brought forward considerable evidence to show that the constitution of the substance is $\text{HgO} \cdot \text{HgCl}_2 \cdot 2\text{NH}_3$ (III) and that it represents a particular member of a general series $x\text{HgO} \cdot (1-x)(\text{HgCl}_2 \cdot 2\text{NH}_3)$ formed by the hydrolysis (during preparation) of fusible white precipitate, $\text{HgCl}_2 \cdot 2\text{NH}_3$.

Britton and Wilson's arguments were based on conductometric and electrometric titrations and analysis; and it was thought that further evidence should be obtainable by a study of the thermal decomposition of the substance in comparison with that of related substances of known constitution. The reference substances chosen were the diammines of mercuric chloride and iodide, and the dipyridinium compound of mercuric chloride; the quantities measured were the energies of activation and of decomposition for the loss of ammonia (or of pyridine), and the total weight of ammonia (or of pyridine) lost in each of the stages of the decomposition. The results obtained support Britton and Wilson's formula (III).

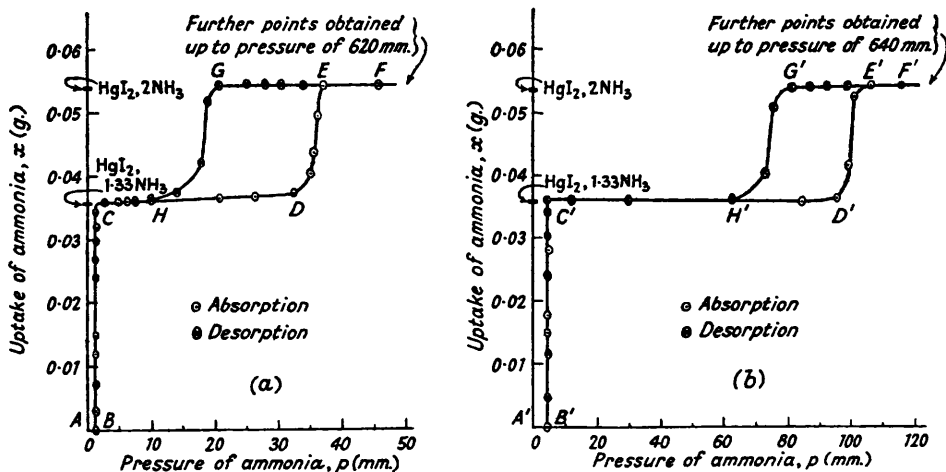
Diamminomercuric Iodide, $\text{HgI}_2 \cdot 2\text{NH}_3$.—When heated, this compound loses its ammonia in two stages (François, *Compt. rend.*, 1899, **129**, 296; 1900, **130**, 572) :



To determine the heat of dissociation $-\Delta H$ for each of these reactions, the dissociation pressure corresponding to each of the systems (i) and (ii) was measured at 20° and at 40° , and the value of $-\Delta H$ calculated by van't Hoff's isochore: x was plotted against p , where x is the content of ammonia in the solid phase, and p the pressure of ammonia in equilibrium with the solid phase. From the stepped isotherms obtained, the value of the dissociation pressure p_d could be read off.

From the experimental point of view the task is essentially one of determining a sorption isotherm, and a sorption technique is appropriate. The electrical sorption balance already described by one of us (*J.*, 1946, 561) was used, together with suitable attachments which permitted the balance case to be evacuated and gas to be admitted to it in a controlled manner (Gregg and Sing, *J. Phys. Coll. Chem.*, 1951, 55, 597); the glass limb surrounding the bucket containing the solid was immersed in a thermostat at the appropriate temperature, and the pressure p was read on a mercury manometer. The resultant isotherms at 20° and 40° are represented in Fig. 1, where the horizontal steps GEF in (a) and $G'E'F'$ in (b) correspond closely to $\text{HgI}_2 \cdot 2\text{NH}_3$, and CHD and $C'H'D'$ to $3\text{HgI}_2 \cdot 4\text{NH}_3$. That the latter steps are not absolutely horizontal is probably due to slight physical adsorption.

FIG. 1.



The reversibility of each reaction was tested by determining the curve both when p was successively increased (p_a), and when it was similarly decreased (p_b); for each of the branches BC and $B'C'$ corresponding to reaction (ii), p_a and p_b agreed within 0.3 mm.; the dissociation pressure $p_d = [(p_a + p_b)/2]$ is 1.3 mm. at 20° and 5.5 mm. at 40° , leading to a value $-\Delta H = 13.2$ kcal. mole $^{-1}$ [cf. 12.9 kcal. mole $^{-1}$ from the data of François (*loc. cit.*)].

With reaction (i) p_a and p_b differed widely and the steps GH and $G'H'$ were not accurately vertical, indicating hysteresis effects. Taking p_d as the value of p_a or of p_b half-way between G and H or between G' and H' —where the isotherms are of maximum slope—gives *two* values for p_d at each temperature [*viz.*, 18.5 and 35.5 mm. at 20° and 75.0 and 100 mm. at 40°], and two estimates of $-\Delta H$, *viz.*, 10.0 kcal. mole $^{-1}$ from p_a and 13.0 kcal. mole $^{-1}$ from p_b [cf. 11.4 kcal. mole $^{-1}$ from the data of François (*loc. cit.*)].

For calculation of the energy of activation E , it was necessary to determine the kinetics of each of the isothermal decompositions (i) and (ii) at two neighbouring temperatures. By analysis of the resultant curves of "weight decomposed" against "time" a measure of the *rate* of the decomposition at each temperature can be obtained; and the energy E can then be calculated from the usual Arrhenius formula, $[RT_1T_2/(T_2 - T_1)] \ln r_2/r_1$ ($r_2 =$ rate at temperature T_2 , $r_1 =$ rate at temperature T_1).

The apparatus was exactly as before, a specimen of the diammine being contained in the bucket. To minimise the variation in "activity" of the solid from one run to another, the diammine for each run was obtained by ammoniating *in situ* the mercuric iodide from

the previous run by exposure to ammonia at 1 atm. for 12 hr. at the temperature of the run. The sample for the first run was obtained by decomposing and reammoniating a sample of the ammine prepared in the wet way.

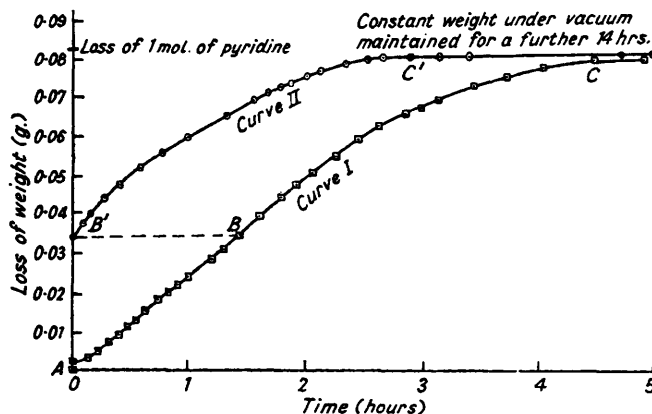
During stage (i) the pressure of ammonia in the apparatus was kept just above the dissociation pressure of stage (ii) in order to prevent the intrusion of the latter; during stage (ii) the system was kept evacuated in the usual manner by a mercury-diffusion pump.

Analysis of the curve of "loss of weight" against "time" showed that the decomposition obeyed with reasonable accuracy, over the range 10–90% of the complete reaction, the equation

$$(w/w_0)^{1-n} = -kt + a \quad \dots \quad (1)$$

where w_0 and w are the weights of NH_3 present in the sample initially and at time t respectively, and a is a constant close to zero. Writing equation (1) in the differential form $-d(w/w_0)/dt = (k/1-n)(w/w_0)^n$, one sees that the order of the reaction is n . The index $(1-n)$ was evaluated by plotting $(w/w_0)^{1-n}$ for a series of values of $(1-n)$ and choosing that which gave the best straight line (cf. Britton, Gregg, and Winsor, *Trans. Faraday Soc.*, 1952, 48, 63); this gave $(1-n) = 0.17 \pm 0.04$, corresponding to an order of $0.83 \pm$

FIG. 2.



0.04. It thus seems probable that the reaction proceeds at an advancing interface, which ideally would give $n = 0.67$, but is liable to disturbing effects which cause deviations of n from this ideal value (cf. *idem, ibid.*; Gregg and Razouk, *J.*, 1949, S 36). The presence of an interface was, indeed, visible to the naked eye in partly decomposed samples.

The value of k can be read off as the slope of the plot of equation (1), and the value of E calculated from the ratio k_{40}/k_{20} ($=r_2/r_1$) by the Arrhenius expression. This gave $E_1 = 17.4$ kcal. mole⁻¹ for reaction (i), and $E_{ii} = 17.5$ kcal. mole⁻¹ for reaction (ii).

Dipyridinomercuric Chloride, $\text{HgCl}_2 \cdot 2\text{py}$.—With this substance the measurements were confined to the kinetics of decomposition. Four runs were carried out, two at 20° and two at 40°, with samples weighing 0.5000 g. each. The curve for the first experiment at 20° is given in Fig. 2 (Curve I), whence it will be seen that the flattening at C occurs when the loss of weight corresponds closely to the formation of the monopyridinium derivative $\text{HgCl}_2 \cdot \text{py}$. [This was confirmed by analysis of the residue of the experiment (Found: Hg, 56.9; Cl, 20.1; $\text{C}_5\text{H}_5\text{N}$, by titration, 22.7. Calc. for $\text{HgCl}_2 \cdot \text{C}_5\text{H}_5\text{N}$: Hg, 57.2; Cl, 20.2; $\text{C}_5\text{H}_5\text{N}$, 22.6%).] The residue had m. p. 194–195° (cf. 193–194° for $\text{HgCl}_2 \cdot \text{C}_5\text{H}_5\text{N}$ prepared as described on p. 1498).

The sigmoid character of Curve I, Fig. 2, indicates that decomposition nuclei are being formed over the initial part, AB, where the slope is increasing with time (Garner, *J.*, 1930, 47; Hume and Colvin, *Proc. Roy. Soc.*, 1931, 132, A, 548). At B the rate begins to diminish, indicating that nucleation is drawing to an end, a suggestion that was confirmed by a further experiment: a sample of the $\text{HgCl}_2 \cdot 2\text{py}$ was rapidly nucleated by exposing it to

vacuum at 60° till the fraction of weight lost was the same as that at *B* in Curve I; the solid was then rapidly cooled to 20° in presence of air, and the system rapidly evacuated, whereupon decomposition recommenced. The curve obtained (Curve II) for the decomposition *in vacuo* at this lower temperature could be almost perfectly superposed on the portion *BC* of Curve I, showing that the effect of nucleation on the rate of decomposition can be ignored once the point of inflection *B* has been passed. In the remaining experiments, therefore, the solid was activated by heating it *in vacuo* for a short time at 60°, and admitting air and cooling it to 20° (or 40°) before pumping was recommenced.

The decomposition—once the point of inflection has been passed—is again represented by equation (1), with $n = 0.67 \pm 0.03$. The energy of activation calculated from the values of k at 20° and at 40° is $E = 15.3$ kcal. mole⁻¹.

An attempt was made to determine the value of E for the loss of quinoline from diquinolinomercuric chloride, $\text{HgCl}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$. Similar results were obtained, but whereas the value of n was *ca.* 0.67 at 60°, it was *ca.* 0.80 at 80°. The change of index made it impossible to insert k_2/k_1 for r_2/r_1 in the Arrhenius equation; instead r_2 and r_1 were taken as equal to the slopes at 40° and 20°, respectively, of the curve of w against t for a given fraction (w/w_0) decomposed. The value of E varied considerably according to the amount decomposed; consequently, the true value of this quantity is uncertain, but it is satisfactory that the range of values found—22.3—15.4 kcal. mole⁻¹ as the loss rose from 0.25 to 0.90 mole of quinoline per mole of HgCl_2 —is of the same order as E for the pyridinium compound.

Fusible White Precipitate, $\text{HgCl}_2 \cdot 2\text{NH}_3$.—The energy of activation for the loss of ammonia was determined from measurements on the sorption balance of the isothermal rate of loss of weight at a succession of temperatures. Since the product of reaction ($3\text{HgCl}_2 \cdot 2\text{NH}_3$) was appreciably volatile at the experimental temperatures, the “bucket” was now made with a drawn-out neck long enough to be above the level of the water in the thermostat; the sublimate then condensed in the neck (plugged with glass-wool as an additional precaution) and its weight was still registered, so the loss in weight was entirely due to the ammonia evolved.

Decomposition *in vacuo* at 147°, 128°, 125°, and 105° gave a curve of loss of weight against time which became horizontal at a loss corresponding to *two-thirds* (not one-half) of the original ammonia content; the residue thereafter slowly sublimed unchanged (condensing in the neck of the container) so that no further loss of weight was registered. The reaction was thus:



and this was confirmed by analysis of the sublimates and the residue (Found, for 125°: NH_3 , 4.07 and 3.98, respectively. Found, for 128°: NH_3 , 4.11 and 3.93. Found, for 147°: NH_3 in residue, 3.94. Calc. for $3\text{HgCl}_2 \cdot 2\text{NH}_3$: NH_3 , 4.01%). The formation of the compound $3\text{HgCl}_2 \cdot 2\text{NH}_3$ in the dry way does not appear to have been reported previously, though Holmes (*J.*, 1918, **113**, 74) obtained a compound of this formula by the action of ammonia gas on an ethereal solution of mercuric chloride and of concentrated solutions of ammonium chloride on infusible white precipitate.

The plot of $w^{\frac{1}{2}}$ against t gave a reasonably good straight line for more than 75% of the course of the decomposition, at all four temperatures; and from the slope of each, the corresponding value of k was calculated [cf. equation (1)]. To evaluate E , the integrated form of the Arrhenius equation was used: $\log_{10} k$ was plotted against $1/T$ and the points for the four temperatures lay on a straight line, from the slope of which $E = 11.4$ kcal. mole⁻¹.

For determination of dissociation pressures corresponding to reaction (iii), a “volumetric” method was used. The solid was contained in a small bulb, *B*, together with a small plug of glass-wool to confine all the sublimate to the bulb; *B* was connected by suitable tubing to a large bulb (250 cm.³) and an ordinary mercury manometer; it was first evacuated by a mercury-diffusion pump with the bulb at room temperature, the connection to the pump was then closed, and a thermostat at temperature T_2 , say, was placed round the bulb. Readings of the pressure were taken until they became constant. To test the reversibility of the decomposition the temperature was raised to T_3 —or some-

times lowered to T_1 —readings of pressure were again taken to constancy, and the temperature moved back to T_2 . The second pressure at T_2 agreed satisfactorily with the first at pressures above 20 mm. (3—4 hr. being required for equilibration), but at lower pressures the two values of p at a given temperature, T_2 , differed by 5 mm. or so, even when (after some 5 hr.) the pressure had become seemingly constant. Accordingly, the values of p_d are not very reliable in the lower pressure range, the sublimation of the product $3\text{HgCl}_2 \cdot 2\text{NH}_3$ being a possible source of error.

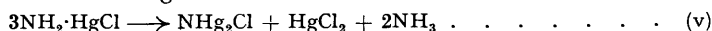
The plot of p against $1/T$ (p being taken as the mean of the values obtained before and after alteration of temperature) gives a good straight line except at the low-pressure end, where as expected there is considerable scatter. From the slope of this line the value $-\Delta H = 21.4$ kcal. mole⁻¹ is obtained.

Infusible White Precipitate.—The rate of decomposition of infusible white precipitate was studied in exactly the same manner as for fusible white precipitate at temperatures of 148°, 155°, and 170°; two runs were conducted *in vacuo* at each temperature, the duplicates showing excellent agreement. In each case there were again indications of a "nucleation" effect in that the rate of decomposition initially increased with time for a short period. The results again fitted with moderate accuracy an equation of the form of equation (1); but in view of the disturbance introduced by the nucleation effect, it was decided to calculate E from the rate r_{40} at 40% decomposition, where the disturbing effect had disappeared, as judged by the form of the isotherm. A plot of the log r_{40} against $1/T$ gave a good straight line, whence the energy of activation was calculated as $E = 20.0$ kcal. mole⁻¹.

The total loss of weight in the experiment varied between 3.15 and 3.25%. This corresponds closely to the calculated weight of ammonia released according to the equation:



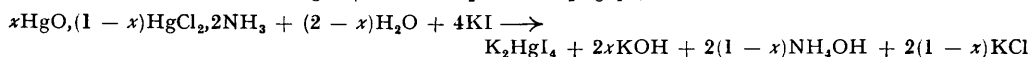
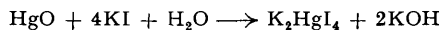
viz., 3.27%. Franklin's formula would give



and this would require a loss, *viz.*, 4.50%, much larger than the experimental figure. Moreover, mercuric chloride sublimes rapidly in air at 150° and *in vacuo* at *ca.* 100°; yet in the present experiments the weight of sublimate caught in the neck of the container was a mere 5% of the initial weight of the sample and this could be accounted for as $\text{HgCl}_2 \cdot 0.67\text{NH}_3$ formed from the small content of fusible white precipitate present as impurity. Actually, Franklin's formula is often given as $\text{NH}_2 \cdot \text{HgCl} \cdot x\text{H}_2\text{O}$ in order to bring it into line with the analytical results; it is seen that the loss of weight would then be even greater than 4.50% as it would include the water.

It was hoped to determine the energy of activation for the loss of the remaining ammonia from infusible white precipitate, after completion of reaction (iv), and the residue from the earlier experiments was accordingly decomposed *in vacuo* at 200° and at 250°, on the sorption balance. Unfortunately, extensive sublimation occurred at both temperatures: in the 200° experiment the composition of the sublimate was very close to $\text{HgCl}_2 \cdot 0.67\text{NH}_3$, whereas for 250° it was $\text{HgCl}_2 \cdot 0.83\text{NH}_3$ in one experiment and $\text{HgCl}_2 \cdot 0.95\text{NH}_3$ in the other, indicating that the sublimate was now a mixture of $\text{HgCl}_2 \cdot 0.67\text{NH}_3$ with $\text{HgCl}_2 \cdot 2\text{NH}_3$. Owing to this complication it was not possible to calculate the value of E ; but the experiments provide further, indirect, support for Britton and Wilson's formula, inasmuch as neither Franklin's nor Rammelsberg's formula can account for the formation of an ammoniated sublimate when the solid product of reaction (iv) is heated *in vacuo*.

Additional evidence is furnished by the results of determinations of the content of "basic" mercury (say Hg_B) before and after the decomposition of infusible white precipitate *in vacuo*; the method used was treatment with potassium iodide and titration with acid of the liberated potassium hydroxide and ammonia (cf. Britton and Wilson, *J.*, 1933, 9):



1498 *Infusible White Precipitate: New Evidence as to its Structure.*

The content of Hg_B in a 2.000-g. specimen was 0.797 g. before, and 0.790 g. after, such decomposition at 155° ; a second specimen, also 2.000 g., gave 0.773 g. of Hg_B after decomposition at 250° . Thus within experimental limits the content of basic mercury is unchanged by the decomposition *in vacuo*, and this strongly supports the "basic chloride" type of constitution, $\text{HgO}, \text{HgCl}_2, 2\text{NH}_3$.

Conclusion.—The values now obtained for E and $-\Delta H$ (kcal. per mole of NH_3) are summarised herewith:

(i) $3(\text{HgI}_2, 2\text{NH}_3) \longrightarrow 3\text{HgI}_2, 4\text{NH}_3 + 2\text{NH}_3$	$E = 17.4, -\Delta H = 10.0-13.0$
(ii) $3\text{HgI}_2, 4\text{NH}_3 \longrightarrow 3\text{HgI}_2 + 4\text{NH}_3$	$E = 17.5, -\Delta H = 13.2$
(iii) $\text{HgCl}_2, \text{py}_2 \longrightarrow \text{HgCl}_2, \text{py} + \text{py}$	$E = 15.3$
(iv) $3(\text{HgCl}_2, 2\text{NH}_3) \longrightarrow 3\text{HgCl}_2, 2\text{NH}_3 + 4\text{NH}_3$	$E = 11.4, -\Delta H = 26.4$
(v) Loss of 1NH_3 from infusible white precipitate	$E = 20.0$

The value of E for infusible white precipitate is thus of the same order as the value of $-\Delta H$ and of E for reactions (i)–(iv) in which either ammonia, or a substituted ammonia, is released by the rupture of a co-ordinate link between a mercury atom and a nitrogen atom. Moreover, the values of $-\Delta H$ just quoted are of the same order as those for the loss of ammonia from the amines of the halides of metals other than mercury. They are too numerous to quote in detail, but may be summarised as follows (in kcal. mole⁻¹): PbX_2 , 11.3–15.6; ZnX_2 , 19.4–25.0; CdCl_2 , 18.6; SnX_2 , 13.3–27.2; CaCl_2 , 15.0; CuX , 10.4–16.7; AgX , 10.7–11.1 ($X = \text{Cl, Br, or I}$) (cf. Biltz *et al.*, *Z. phys. Chem.*, 1909, **67**, 578; *Z. anorg. Chem.*, 1920, **114**, 174; 1921, **119**, 27; 1922, **124**, 230; 1923, **129**, 161, 230; **130**, 93; Glasson, Thesis, London, 1949, p. 169). Hart and Partington (*J.*, 1943, 104) give results for the amines of various halides of Ca, Ba, Ni, Li, Na, Fe^{II} , Mn^{II} , and Cu^{II} , and 31 values lie between 9.86 and 19.38, one being 24.3.

These facts support formula (III) as against (I); if the latter were correct, the value of E for infusible white precipitate should lie distinctly higher than the values of E and of $-\Delta H$ for the amines, since the loss of an ammonia molecule would involve an interaction between two NH_2 groups, attached to separate mercury atoms, and should indeed be comparable with that for the loss of ammonia from a metallic *amide*. There are no data permitting the calculation of E for the decomposition of metal amides, but figures are available for the heats of formation (cf. I.C.T., Vol. 5, pp. 196 *et seq.*), whence $-\Delta H$ may be calculated for the amides of Ca, Sr, Ba, and Li as 30.3, 27.8, 25.4, and 35.2 kcal. mole⁻¹, respectively. As expected, these are higher than any of the values quoted for the amines, and considerably higher than most of them. For the same metal, Ca, the difference is particularly striking: the value for the amide, 30.3 kcal. mole⁻¹, is nearly twice as high as that for the ammine in the reaction $\text{CaCl}_2, 2\text{NH}_3 \longrightarrow \text{CaCl}_2, \text{NH}_3 + \text{NH}_3$, *viz.*, $-\Delta H = 15.3$ kcal. mole⁻¹ (cf. Hüttig, *Z. anorg. Chem.*, 1922, **123**, 317).

The data for E do not permit a decision between (II) and (III), for in the absence of reference substances definitely known to contain the NHg_2 grouping it is not possible to estimate $-\Delta H$ or E corresponding to Rammelsberg's formula. However, the data for the loss of weight on heating correspond definitely to the reaction $\text{HgO}, \text{HgCl}_2, 2\text{NH}_3 \longrightarrow \text{HgO}, \text{HgCl}_2, \text{NH}_3 + \text{NH}_3$ rather than to $3\text{Hg} \cdot \text{NH}_2\text{Cl} \longrightarrow \text{NHg}_2\text{Cl} + \text{HgCl}_2 + \text{NH}_3$ or to $\text{NHg}_2\text{Cl}, \text{NH}_4\text{Cl} \longrightarrow \text{NHg}_2\text{Cl} + \text{NH}_3 + \text{HCl}$, and so again support (III). Finally, the fact that there is no change in the content of "basic" mercury is strong confirmation of Britton and Wilson's formula (III).

EXPERIMENTAL

Preparation of Materials.—*Diamminomercuric iodide.* This was prepared by Saha and Choudhury's method (*Z. anorg. Chem.*, 1912, **77**, 41) (Found: Hg, 41.14, 41.22; I, 52.24, 52.08; NH_3 , 6.84, 6.91. Calc. for $\text{HgI}_2, 2\text{NH}_3$: Hg, 41.07; I, 51.96; NH_3 , 6.97%).

Dipyridinomercuric chloride. Mercuric chloride (50 g.) was warmed with redistilled pyridine (100 ml.) until complete solution was obtained. On cooling, white crystals formed which were filtered off, washed with a little pyridine, and rapidly dried with filter-paper. The product was stored on porous tile in a desiccator (freshly calcined CaO); m. p. 108° (rapid heating) (Schroeder, *Z. anorg. Chem.*, 1905, **44**, 11, gives 103° ; Ströholm, *ibid.*, 1908, **57**, 106, gives 108°). Analysis (Found: Hg, 47.7, 47.8; Cl, 16.9, 16.8; $\text{C}_5\text{H}_5\text{N}$, 35.0, 35.15%; $\text{Hg}:\text{Cl} =$

[1953] *Aminophenoxazines as Possible Antitubercular Agents. Part I.* 1499

1 : 1.997. Calc. for $\text{HgCl}_2 \cdot 1.88\text{C}_5\text{H}_5\text{N}$: Hg, 47.8; Cl, 17.0; $\text{C}_5\text{H}_5\text{N}$, 35.4%) showed some decomposition.

Fusible white precipitate. 200 C.c. of a solution of 4.5N-ammonia containing 30 g. of ammonium chloride were heated to boiling, and a solution of mercuric chloride (50 g./l.) was added dropwise, with stirring, until the precipitate first formed after the addition of each drop just did not dissolve on stirring. The whole was then cooled, and the crystals were filtered off, washed with acetone, and dried at room temperature in a desiccator (Found: Hg, 65.4; Cl, 23.3, 23.5; NH_3 , 11.2, 11.05. Calc. for $\text{HgCl}_2 \cdot 2\text{NH}_3$: Hg, 65.6; Cl, 23.1; NH_3 , 11.15%).

Infusible white precipitate. The method of B.P., 1914, was adopted (Found: Hg, 77.1, 77.2; Cl, 13.4, 13.2; NH_3 , 6.7, 6.7. Calc. for $\text{NH}_2 \cdot \text{HgCl}$: Hg, 79.6; Cl, 14.1; N, expressed as NH_3 , 6.75%. Calc. for $\text{HgO} \cdot \text{HgCl}_2 \cdot 2\text{NH}_3$: Hg, 76.8; Cl, 13.6; NH_3 , 6.5%).

Our thanks are offered to Professor H. T. S. Britton for bringing this problem to our attention and for his constant encouragement. One of us (D. R. G.) acknowledges the receipt of a maintenance grant from the Department of Scientific and Industrial Research, and a College Research Scholarship.

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[Received, November 20th, 1952.]
