REACTION OF AMINES WITH SULFUR DIOXIDE. I. ANILINE AND SULFUR DIOXIDE

BY ARTHUR E. HILL

In the year 1909 experiments were conducted in this Laboratory in an effort to study the reactions of acid anhydrides upon basic anhydrides, by Mr. William A. H. Zink and myself. It was found that sulfur dioxide combines readily with aniline, either pure or in solution in anhydrous solvents, giving crystalline yellow compounds with moderately high dissociation pressures; the same type of reaction occurs with the toluidines, with benzidine, with dimethylaniline and with any amine of a fairly pronounced basic character; the reaction appears to be quite general. Because of the partial decomposition and loss of sulfur dioxide which these compounds underwent during handling, it was not found possible to analyze them by the usual methods, and the work was therefore stopped. During the past year the work was taken up again and the composition of the compounds determined by the phase rule methods made familiar in the early study of the hydrates of copper sulfate and more recently by Bancroft[1] in his studies of salt formation among the proteins; vapor pressure measurements have been made and a study made of the behavior of the compounds upon melting.

Search of the literature has disclosed that previous to our investigation only a single case had been found in which this general reaction figures, namely, that of sulfur dioxide with aniline, and in this instance the facts are given correctly in part and quite incorrectly in other parts. Schiff[2] states, incidentally to his work upon organic amines, that "aniline absorbs sulfur dioxide, as previously noted by Hofmann," that the solid is yellow, appears to contain equivalent amounts of both substances, i. e., has the formula $C_6H_5NH_2 \cdot SO_2$ and can exist only in presence of excess sulfur dioxide; the reference to Hofmann's work has not been located. On exposure to the air, the solid became quickly decolorized with loss of sulfur dioxide, changing to what he believed to be $2C_6H_5NH_2 \cdot SO_2$; his analysis gave 26–28% SO_2, the theory requiring 25.6%; the original yellow solid he did not analyze. Boessneck[3] mentions the original compound and found it to contain 32% SO_2, where the theory requires 40.8% for a 1:1 compound. Michaelis[4] by treating thionyl aniline (C_6H_5NSO) with aniline and water or with moist ether obtained the second of Schiff's compounds, the white solid said to be $2C_6H_5NH_2 \cdot SO_2$, melting at about 60°, and only slowly decom-
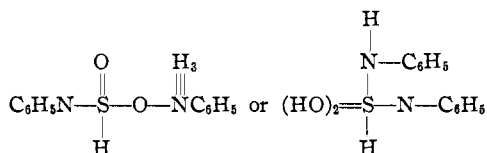
[1] Bancroft and co-workers, J. Phys. Chem., **34**, 449, 753, 1217, 1930, 2433 (1930).

[2] Schiff, Ann., **140**, 125 (1866).

[3] Boessneck, Ber., **21**, 1910 (1888).

[4] Michaelis, ibid., **24**, 749 (1891).

posing into its components; he proposes the structural formula of a phenyl-amidosulfinic acid for the yellow compound, and

$$C_6H_5N\underset{H}{\overset{O}{\underset{|}{\overset{||}{-}}}}S-O-\overset{H_3}{\overset{|||}{N}}C_6H_5 \text{ or } (HO)_2=\underset{H}{\overset{N-C_6H_5}{\underset{|}{\overset{|}{S}}}}-N-C_6H_5$$

for the second. Schiff also records that if sulfur dioxide is passed into a mixture of aniline and water, a heavy precipitate of a *yellow* crystalline body is obtained, which will lose sulfur dioxide rapidly until it has reached the composition $4C_6H_5NH_2 \cdot SO_2 + n$ aq., which compound he regards as belonging to the class of the sulfites of aniline, no analysis being given.

Subsequent to our earlier work, Korezyński and Glebocka[5] investigated the action of sulfur dioxide upon a large number of amines and substantiated the formulas of the resulting compounds by the volume of sulfur dioxide absorbed under one atmosphere pressure. In the majority of the cases, although not in all, the ratio of one mole of sulfur·dioxide to one amino group was observed. The dissociation pressures of these compounds were not measured.

The results which follow in this paper have established that sulfur dioxide acts upon anhydrous aniline to form only the yellow addition product $C_6H_5NH_2 \cdot SO_2$, for which neither Schiff nor Boessneck could obtain a satisfactory analysis; that its exposure to the air results not only in the loss eventually of some of the sulfur dioxide, but also in the absorption of water with the formation of a white crystalline mass which is a mixture of the acid sulfite and the normal sulfite, the two true salts formed by aniline and sulfurous acid; the other formulas proposed by Schiff, Boessneck and Michaelis are not substantiated, and the yellow color of Schiff's compound obtained in the presence of water may be taken as evidence that this material held considerable quantities of discolored aniline. It should be remarked that in looking for descriptions of the salts of aniline and other amines with sulfurous acid, it was found that Beilstein's earlier edition, while giving in general the salts with hydrochloric acid, sulfuric acid, nitric acid, etc., gives no evidence that the salts of sulfurous acid have been prepared; the edition now being completed has not yet reached the volume on the aromatic amines. The generalization may be made, on the basis of this work, that amines form yellow addition products usually in the 1:1 ratio with dry sulfur dioxide, and that in the presence of water, as should be expected, normal or acid sulfites are produced, which are, of course, colorless.

For the preparation and study of the addition compound, Kahlbaum's aniline was used, redistilled and stored in a desiccator over sulfuric acid; the sulfur dioxide was

5 Korezyński and Glebocka, *Gazz. chim. ital.*, **50**, I, 378 (1920).

taken from a small commercial cylinder, which was allowed to run for a considerable time to free the gas from possible impurities. For the vapor pressure measurements by which the composition of the compound was determined, the apparatus consisted of a glass· stoppered 50-cc. distilling flask immersed in a water thermostat, connected by its side tube to a 50-cc. gas buret from which it could be shut off by a glass stopcock, and also connected to a mercury manometer and to a Hyvac pump shut off by a mercury-sealed stopcock. The aniline and sulfur dioxide, therefore, were in contact only with glass throughout the entire apparatus. Samples of about one gram of aniline were weighed into the reaction vessel for each run, with the addition of glass beads to increase the surface. After introduction of the aniline the system was connected with the pump, which in less than sixty seconds reduced the pressure to an amount too low to be noted by direct reading on the manometer. For the introduction of known amounts of sulfur dioxide, the gas buret was fitted with a side tube and a three-way stopcock; in filling the buret, the cylinder of sulfur dioxide was connected by rubber tubing to the three-way stopcock and the gas, previously dried by sulfuric acid in a small U-tube, passed through the by-pass to sweep out air for about twenty minutes. It was then turned into the gas-buret and allowed to displace the mercury with which the buret had been filled, care being taken that the gas entered always under a slight excess pressure so that possible leakage of air inward through the rubber tubing was eliminated. By calculation from the volume, pressure and temperature of the gas the weight admitted to the system was known. The initial absorption of the gas by the aniline is very rapid, and equilibrium appears to be reached within a few hours up to the point where the liquid has been largely changed to the solid, at which time entrance of the gas through the crust of solid is slowed up considerably; twenty-four hours were allowed to elapse before final readings of the manometer were made. By making correction for the amount of sulfur dioxide remaining in the apparatus, of known volume, pressure and temperature, the amount absorbed by the aniline could be calculated; these corrections are of relatively small amount only, since the total volume of the apparatus was only 92 cc. and the pressures are low. The probable errors in the reading of the manometer with the correction for variations in barometric pressure are of the order of ±0.5 mm. of mercury. The results of such a run are given in Table I.

TABLE I

VAPOR PRESSURE OF ANILINE + SO$_2$ AT 25°

Weight of aniline used, 1.311 g.

Pressure, mm.	SO$_2$ absorbed, mg.	Moles of SO$_2$ absorbed per mole of aniline
17.5	49.4	0.055
37.0	99.2	.110
44.2	130.9	.145
44.2	247.1	.274
44.0	379.7	.421
45.7	596.9	.668
45.5	824.1	.914
56.0	885.5	.981
127.5	887.6	.984
475.5	888.2	.985
43.0	(Partial evacuation)	

From the plot of these results in Fig. 1 the interpretation can easily be made. Sulfur dioxide dissolves in liquid aniline at 25° up to a pressure of about 44 mm. and a concentration of about 0.14 mol of the gas per mole of

aniline. At this concentration the solid addition product appears and the system, with three phases and a fixed temperature, remains invariant upon further additions of sulfur dioxide until the aniline has been completely converted into the compound, at which point further additions of gas cause an abrupt rise in pressure without further absorption in significant amount. The abrupt rise at an absorption of 0.98 mole is sufficient proof that the components combine in a 1:1 ratio to form the compound $C_2H_5NH_2 \cdot SO_2$, and the absence of any break in the flat portion of the curve rules out the existence of any of the compounds lower in sulfur dioxide content assumed by Schiff and Boessneck. The slight rise which is noted in the nearly flat portion of the curve is due, it is believed, not to impurities in the gas but to incomplete attainment of equilibrium from the higher pressures, impeded by the crust of solid upon the liquid; partial evacuation, as shown in the last line of the table, gave a pressure as low as 43 mm., while the same sample, after the higher temperature and higher pressure of Table II, showed a pressure slightly over 44 mm.

Fig. 1.—Pressure–composition diagram, aniline + SO_2 at 25°.

The color changes in this system are marked, and appear to be alike for all the amines upon treatment with sulfur dioxide. The liquid solution obtained from colorless aniline has a deep orange-red color, which appears also upon melting the solid in a sealed vessel; while the solid compound, if freed from all solution, and especially if sublimed, is of a lemon-yellow color.

Vapor pressure measurements were made at several temperatures by first exhausting the system below 43 mm. to insure absence of excess sulfur dioxide and then changing the temperature of the thermostat. At the higher temperatures equilibrium appeared to be reached in fifteen to thirty minutes. The results are given in Table II.

The vapor pressure curve, shown in Fig. 2, rises very steeply with the temperature. A plot of the logarithm of the pressure with the inverse of the absolute temperature, shown in Fig. 3, gives a good straight line, in which only the point at 3.5° appears misplaced. From this curve it ap-
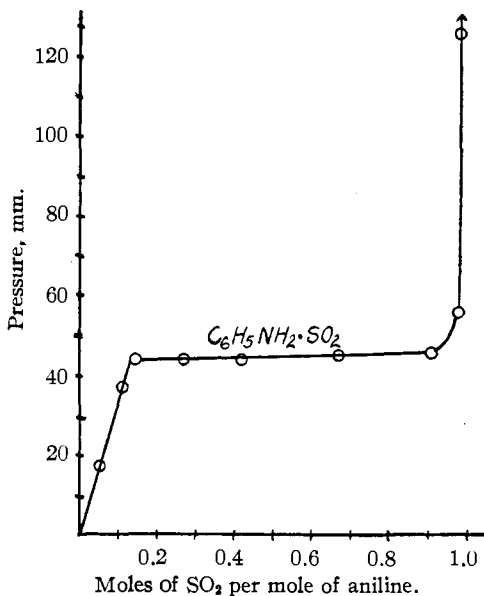
TABLE II

VAPOR PRESSURE OF $C_6H_5NH_2 \cdot SO_2$ AT VARYING TEMPERATURES

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
3.5	3.7	45	360
25	43	50	630
30	72.5	52	(760) (by extrapolation)
35	125		

pears by extrapolation that the pressure reaches 760 mm. at a temperature of 52°, as given in the last line of Table II. The true melting point of the compound is distinctly higher, so that it would sublime without melting under atmo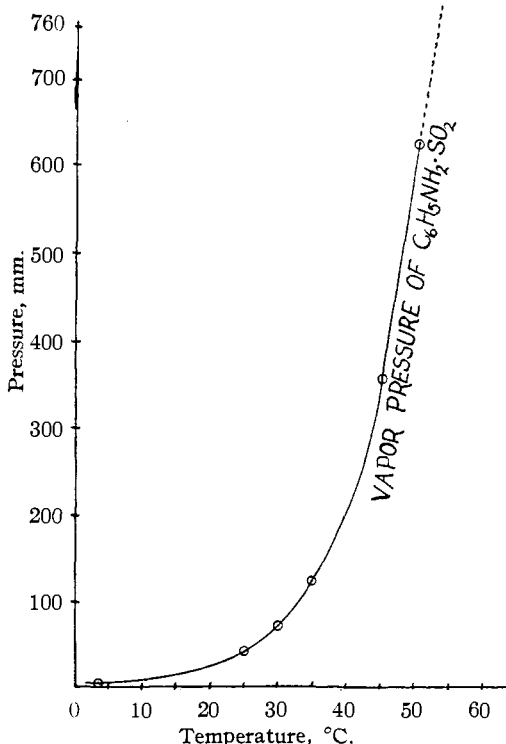spheric pressure. From the slope of the curve of Fig. 3 the heat of vaporization of the compound, calculated from the formula $d \ln p/d\ T = \lambda/RT^2$, is 19,630 cal.

Fig. 2.—Vapor pressure of $C_6H_5NH_2 \cdot SO_2$ at varying temperatures.

Efforts to find the melting point of the compound gave only approximate results. The work, of course, must be conducted in a closed system, to prevent loss of sulfur dioxide. Because of the high pressures developed, only small amounts could be safely handled, and it was not found possible to keep the composition entirely under control. Amounts of 200 to 500 mg. of aniline were weighed into small tubes of total capacity of 2 to 3 cc. and dry sulfur dioxide introduced through a capillary; the tubes were sealed and reweighed to ascertain the amount of sulfur dioxide present, but in no case could the amount be brought up to the requisite one molecule. Samples holding over 90% of this amount came to complete liquefaction at temperatures slightly over 60°; the best sample, containing 0.969 mole of sulfur dioxide per mole of aniline, melted completely at 63.1°. If we assume that the melting point curve of this system forms a blunt angle with the composition axis, as should be true for a compound which dissociates largely into its com-

ponents, the melting point cannot be greatly higher than the temperature found, and may be set at about 65° and a pressure of about 3.5 atmospheres, from the curve of Fig. 3.

Inspection of Fig. 1, which is a pressure–composition isotherm for 25°, will show that for higher temperatures, since the solubility of the solid in liquid aniline increases, the horizontal section of the curve will become shorter, until it reaches the dimensions of a point and a position at 1:1 composition on the ordinate at the congruent melting point, where the composition of liquid phase and solid phase is the same. A search was made to find some treatment in the literature which should include the effect of the three variables, temperature, pressure and composition, upon a compound having a congruent melting point. Such a treatment is not in Roozeboom's "Die Heterogenen Gleichgewichte," and I have not found it elsewhere. For that reason it seemed worth while to construct a model showing these relationships so that they can be easily visualized; Fig. 4 is a perspective view of such a model, including the three variables and showing the regions of stability for the solid, liquid and gaseous phases. Though drawn to illustrate the system aniline–sulfur dioxide,
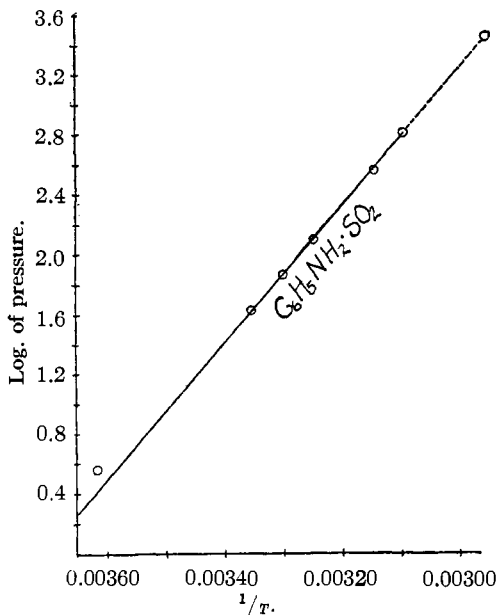

Fig. 3.—Log of pressure $vs.$ $1/T$ for $C_6H_5NH_2 \cdot SO_2$.

it may be applied without change to any binary system forming a compound which melts congruently, at temperatures above the melting points of the two components. The curve bge will be recognized at once as the solubility curve for the compound, which in the representation of condensed systems is familiarly drawn as a projection upon the composition–temperature surface. What is left out of the familiar projection, however, is that not only is the solubility curve bg moving in the direction of higher pressures with increase in temperature, but that ge also is moving in the direction of higher pressures with $decrease$ in temperature. To the well-known fact that the solid phase may be in equilibrium at a constant temperature with either of two liquid phases of differing composition ($i. e.$, has two solubilities) is to be added the fact that, of course, the two liquids have different vapor pres-

sures. The front view of the figure, here given, shows in perspective the regions of stability for the solid, for liquid solution and for vapor alone.

The projection of an isotherm such as t_0 upon the composition–pressure surface is shown in Fig. 5. This is a complete representation of what has been shown in part in Fig. 1 and in the usual representation of vapor pressures in two-component systems. The line ab, shown in both Fig. 5 and Fig. 1, represents the change in solubility of sulfur dioxide in liquid aniline with increase in pressure; at pressures lower than b the system can consist only of a liquid phase conjugate with vapor of the same pressure and a different composition, expressed by a point on the vapor curve $axyf$. At
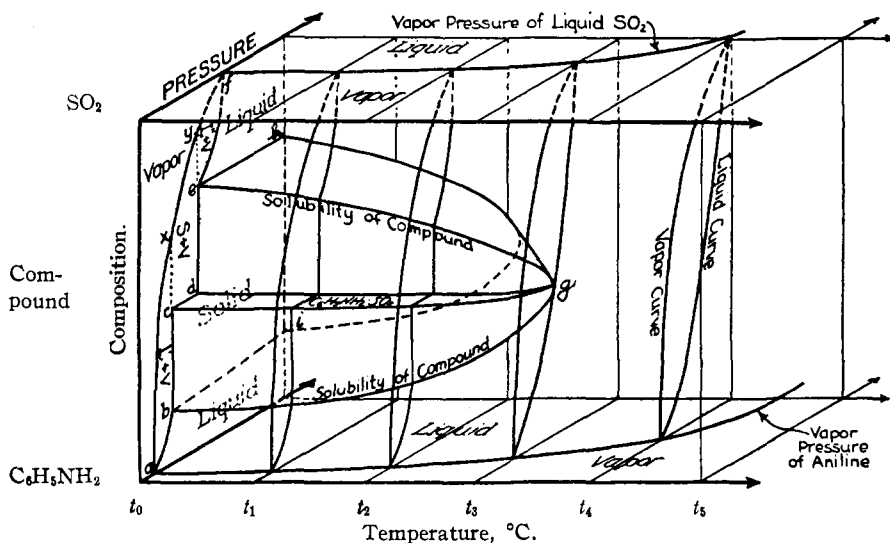

Fig. 4.—Pressure–temperature–composition diagram for a compound with congruent melting point.

the pressure b solid appears, and addition of sulfur dioxide results only in variation in the amounts of the three invariant phases, b (liquid), c (solid compound) and x (vapor). Upon addition of sulfur dioxide up to the composition c the liquid has all been changed to solid compound; further additions of sulfur dioxide result only in a change in pressure without any change in composition of the compound, $i.\ e.$, the system is isothermally univariant and consists of solid conjugate with vapor of the compositions shown along the section xy of the vapor curve. At d, a high pressure not measured in this instance, there is condensation of a new liquid phase e, rich in liquid sulfur dioxide, and the system is again isothermally invariant, consisting of compound, liquid phase e and gaseous phase y. Additions of sulfur dioxide result now in diminishing the amount of the solid and increasing the amount of the liquid until the solid disappears entirely at e; further addi-

tions give the isothermally univariant system consisting of liquid represented on the curve ef and vapor represented on the curve yf. The pressure at d may be looked upon not only as the second vapor pressure of the system compound–liquid–vapor, but also as the deliquescence pressure of the compound. The curves bi and eh are boundary curves between the area for the solid and the areas for the two liquid phases; they will tend to meet at high pressures or to separate further according as the volume of the system tends to decrease or increase upon dissolving of solid phases. If isotherms are drawn at successively higher temperatures, the distance cd and the distances bc and de will become shorter; at the congruent melting point the four points will have met at a single point, represented by g in Fig. 4. Above this temperature only liquid and vapor can exist, up to the point where the vapor curve and the liquid curves meet, at the critical temperatures for varying solutions of the two liquids.

Experimental work has also been carried out upon the ternary system consisting of aniline, sulfur dioxide and water, in order to determine whether or not normal sulfites and acid sulfites exist, and to explain the observation that the yellow addition product previously discussed turns white on exposure to the air. It is possible to determine the composition of ternary systems such as this

Fig. 5.—Pressure–composition diagram for a compound with congruent melting point.

by the measurement of vapor pressures as used above, but not with the same simplicity either as to theory or as to practice. Considering that aniline and water have but small mutual solubility, it becomes clear that the addition of sulfur dioxide will, upon the appearance of solid sulfite, give rise to an isothermally invariant system consisting of two liquids, solid and vapor; but in the absence of previous knowledge as to the solubility of the solid in the liquids, it is impossible to predict just what quantities of the two liquids should be taken to insure the appearance of the solid. Again, the absorption of the gas without increase of pressure will not cease abruptly at the point where the composition of the solid is reached, because of the solubility of gas in the liquid phase, but by keeping this liquid at a minimum the amount of this correction can be minimized. Another isothermally invariant system will consist of solution, vapor,
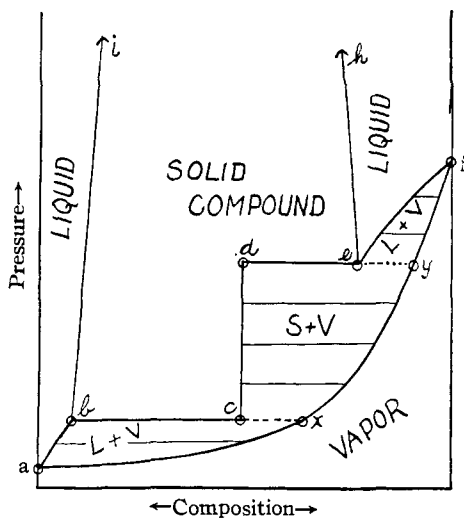
solid normal sulfite and solid acid sulfite, if the solubility relations can be properly controlled, with the same error in determining the composition due to absorption of excess gas by the liquid phase. The experiments were therefore begun with aniline and a quantity of water only slightly in excess of the one mole required for the reaction. It was found in this case, and in others in which the water was increased by successive amounts up to eight moles, that the initial absorption of sulfur dioxide was rapid and that an approximately constant pressure was obtained, but that when the absorption had reached from 0.6 to 0.8 mole it ceased quite abruptly and that high pressures allowed to remain in contact with the system for periods up to two weeks caused no further absorption in significant amount. It is believed that this behavior is due solely to mechanical obstruction; that the salt, forming a hard and impenetrable crust in an apparatus in which agitation is almost impossible, acts as a barrier between the water and the gas, and that the reaction with water present only as a vapor is too slow to be followed. This hypothesis was justified by the results of experiments in which larger amounts of water were used, of which the results are given in Table III.

TABLE III

ANILINE, SULFUR DIOXIDE AND WATER AT 20°

Curve 1		Curve 2	
Molar ratio, aniline/water = 34		Ratio = 18.5	
Wt. of aniline 0.605 g.		Wt. of aniline 0.594 g.	
Pressure, mm.	Moles SO_2 absorbed per moles aniline	Pressure, mm.	Moles SO_2 absorbed per moles aniline
17.5	0	17.5	0
17.2	0.154	18.0	0.171
17.7	.473	18.5	.486
19.0	.794	18.6	.538
38.0	.960	20.5	.848
80.5	1.055	23.5	.956
		43.4	.997
		84.0	1.03

In calculating the moles of sulfur dioxide absorbed, the assumption was made that its partial pressure in the system was the total pressure minus that of pure water, since the aqueous pressure of the solutions was not known. The error introduced by this assumption can affect the position of the points as shown in Fig. 6 only by a fraction of one per cent. The temperature of 20° was used to avoid the distillation of water into the outer parts of the vessel, which occurred at 25°. The two curves, shown in Fig. 6, show that the gas is absorbed with small continuous rise in pressure up to an amount approximating one mole of sulfur dioxide to one of aniline, the approximation being closer where the amount of excess water is smaller (Curve 2) and the error introduced by its presence smaller; above this ratio of sulfur dioxide to aniline, the absorption increases very slowly with large

increase in pressure and the upright branches of the curve represent an approximation to Henry's law.   In case 1 solid phase appeared at about 0.6 mole of gas present, in case 2 at about 0.3 mole.   The curves may be taken as establishing the existence of the 1:1 compound containing water, which would be the acid sulfite, $C_6H_5NH_3HSO_3$, but give no evidence as to the existence of the normal sulfite or other salts.

The effort to prepare the various sulfites in condition for analysis by precipitation from aqueous solution meets with obstacles because of the difficulty in finding such a drying agent for ternary compounds as would absorb the water from the mother liquor upon the crystals without leading to loss of water of composition.   The nearest approach to such a desiccant is the anhydrous compound, $C_6H_5NH_2$·SO_2, which has been shown capable of combining with water, but it is not the hydrate immediately below the acid salt, $C_6H_5NH_2$·H_2O·SO_2, and therefore is not the correct drying agent for that compound.   It was used, however, with a sample of salt prepared by passing sulfur dioxide to saturation into a 2:3 mixture of aniline and water, from

Fig. 6.—Absorption of sulfur dioxide by aniline in the presence of water at 20°.

which the white salt crystallized copiously.   After rapid centrifuging it was placed in a desiccator over a large amount of the yellow addition product. Loss of weight occurred continuously for thirty-four days, after which the loss dropped to an amount of less than 0.01% per day, which loss doubtless occurred during the transfer of the sample to the balance.   At this point an analysis was made for the SO_2 content, by evolving the gas from a sample by addition of acid and passing it into a known solution of iodine in potassium iodide; the sulfur dioxide content found was 23.46%, which is close to that calculated for the normal sulfite, $(C_6H_5NH_3)_2SO_3$ (23.88%). It appears then that aniline forms a crystalline normal sulfite and a crystalline acid sulfite which may be precipitated from aqueous solutions, but
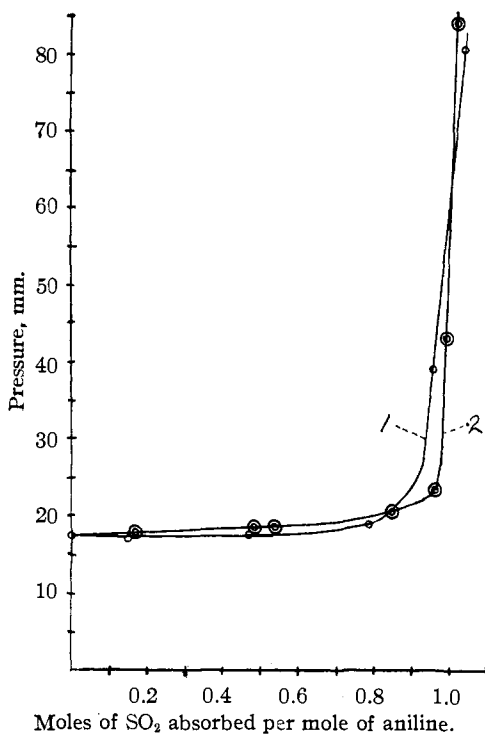
which have (as shown in Table III and what follows) sufficiently high decomposition pressures to prevent their easy preparation in pure form.

The decomposition pressure of the anhydrous addition compound has been shown, in Table I, to be 44 mm. at 25°. That of the acid salt could not be measured, but is some rather small fraction of the 18–20 mm. of Table III at 20°. That of the normal salt was determined at 20° by direct addition of the dry compound to the apparatus and repeated evacuation with the pump: it is found to be 3.5 mm. ±0.5, of which but half is sulfur dioxide. We may therefore explain the action of the yellow compound on exposure to air as an addition of water and a loss of sulfur dioxide passing through the composition of the acid salt to that of the normal salt.

A sample of the normal sulfite, taken in a closed tube with excess sulfur dioxide, melted incompletely to a red liquid, beginning at 62°, in sufficient proximity to the melting point given by Michaelis[4] to make it probable that his white solid was the normal sulfite.

From the high dissociation pressure which the yellow addition product displays, it seems preferable to consider that the sulfur dioxide is held by secondary valence and that the structural formulas proposed are likely to be misleading. However, it was found that when samples are heated in a closed tube at 100° for about sixteen hours, they change to a nearly colorless solid, not liquefying at 100°, and with no appreciable sulfur dioxide pressure. The nature of these compounds will be the subject of further investigation, as will also vapor pressure measurements of the addition products of sulfur dioxide with other aryl amines and the measurement of the solubility of the two sulfites of aniline in water.

Summary

1. Aniline combines with sulfur dioxide in the 1:1 ratio to form a yellow crystalline solid.

2. The vapor tension of the addition compound was measured between 3.5 and 50°, and the heat of dissociation calculated.

3. A diagram has been constructed and discussed for a binary compound above the melting points of its two components, showing temperature, composition and pressure as variables.

4. In the presence of water aniline combines with sulfur dioxide to form a normal sulfite and an acid sulfite, both of which have dissociation pressures markedly less than that of the anhydrous addition compound.

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