[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Compounds of Sulfur Dioxide with Various Amines[1]

BY ARTHUR E. HILL AND THOMAS B. FITZGERALD

The compounds of sulfur dioxide with various amines, first noted by Schiff[2] in 1866, have had but little attention until recently. In 1920 Korezynski and Glebocka[3] showed that formation of these compounds is common to a large group of amines and determined the composition of many of them. Determinations which include not only composition, but also vapor tension and other physical properties, have been carried out by Hill[4] in the case of aniline and by Foote and Fleischer[5] for several aromatic amines.

In the present investigation a series of aromatic and aliphatic amines, after purification by distillation, was treated with measured volumes of sulfur dioxide at constant temperature and the vapor pressures measured; by means of pressure–composition diagrams the composition of the compounds formed was deduced. The vapor pressures were then measured over a range of temperatures, in order that the heats of formation of the compounds could be calculated by the Clausius–Clapeyron formula. The apparatus for the determinations was that described in the previous publication;[4] from these measurements pressure–composition diagrams have been drawn and phase-rule interpretations made. Pressures were read upon a mercury manometer and the admitted volumes of sulfur dioxide read from a gas buret. With either liquid or solid amines, it has been found that the addition of sulfur dioxide usually results in the formation of a crust of solid addition compound which retards further absorption of gas and frequently delays attainment of equilibrium for several weeks, especially when the amount of gas absorbed has approached the total reacting quantity. To lessen this difficulty two devices have been employed. In some cases a non-reacting solvent of low vapor pressure has been used (dibutyl ether); this usually resulted in the formation of a more or less granular precipitation of the addition compound and more rapid attainment of equilibrium. By making an independent measurement of the solubility of sulfur dioxide in the dibutyl ether at various pressures, it was possible to make an approximate correction and so determine the quantity of gas absorbed by the amine and the pressure due to the compound present. In other cases a large glass bulb of known volume (about 500 cc.) was attached to the apparatus which after evacuation could be used to withdraw known volumes of gas. In such cases, the smaller reaction vessel was first rapidly filled with excess sulfur dioxide and after attainment of equilibrium known volumes were taken out, leaving the composition of the residual material known by difference. Neither of these improvements appears to give as rapid or as satisfactory results as the method of Foote and Fleischer,[5] who carried out the reactions at low temperatures in presence of excess liquid sulfur dioxide in which the reactions proceed much more rapidly; it has been our unvarying experience that the equilibrium gas–solid is slow of attainment and very easy of misinterpretation.

The results of the pressure–composition experiments are collected in Table I. The remark "Evac." at the foot of a column indicates that the most probable pressure of the system was taken as that obtained after partial evacuation of the system by means of the attached bulb; the symbol "p" indicates that the pressure taken is that found on direct addition of sulfur dioxide.

When the experiments were conducted in the presence of the dibutyl ether as a solvent (marked "*a*" in Table I), corrections were made for the pressure of that solvent and for the absorption of sulfur dioxide under various pressures in 5 cc. of the liquid, the amount used in the experiments. The data are given in Table II, together with a calculation which shows that the absorption of sulfur dioxide by this liquid follows Henry's law within fairly narrow limits.

Toluidines.—The first four columns of Table I show results for the four toluidines; the curves are shown in Fig. 1. For *o*-toluidine, the theoretically invariant system gave pressures at 25° between 48.7 and 50.3 mm., with large rise after about 0.8 mole absorption of sulfur dioxide (curve 1, Fig. 1); the pressure found upon partial evacua-

---

[1] The material of this paper is from the thesis of Thomas B. Fitzgerald, presented in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1933.

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

[3] Korezynski and Glebocka, *Gazz. chim. ital.*, **50**, I, 378 (1920); *Chem. Abs.*, **15**, 522 (1921).

[4] Hill, THIS JOURNAL, **53**, 2598 (1931).

[5] Foote and Fleischer, *ibid.*, **56**, 870 (1934).

TABLE I

VAPOR PRESSURE COMPOSITION DATA FOR AMINES WITH SULFUR DIOXIDE

Moles of SO_2	Press., mm.
o-Toluidine, 25°	
0.000	1.0
.021	8.0
.049	16.5
.074	29.5
.104	41.5
.140	58.6
.194	86.3
.319	48.7
.459	49.0
.590	50.3
.857	54.0
.978	167.6
.981	221.5
Evac.	48.2
m-Toluidine, 25°	
0.000	2.0
.144	42.5
.324	123.5
.485	228.5
.652	328.8
.848	327.0
.931	349.7
.981	446.0
.994	701.5
Evac.	323.0
m-Toluidine, 15°	
0.000	2.0
.151	25.0
.321	60.0
.485	81.5
.638	81.5
.782	81.0
.920	96.0
.987	130.5
.990	395.0
p	81.0
p-Toluidine in ether,[a] 20°	
0.000	0.0
.138	11.0
.305	13.0
.472	17.0
.639	22.5
.781	31.5
.910	155.0
.938	317.5
.972	477.5
1.000	623.7
p	11.0
Quinoline, 25°	
0.000	2.0
.145	16.3
.222	36.2
0.270	14.0
.429	14.5
.515	12.5
.733	10.5
.861	24.5
.972	57.0
.998	123.0
0.460	47.0
.575	48.2
.780	50.5
.939	62.4
.963	174.1
.982	360.0
Evac.	45.0
o-Phenylenediamine, 25°	
0.023	3.5
.074	4.0
.221	4.0
.325	4.0
.471	4.0
.550	15.4
.646	17.0
.800	16.7
.960	17.5
.963	69.0
.970	740.0
p	4.0
and	17.0
p-Phenylenediamine, 50°	
0.033	16.0
.150	18.0
.310	19.5
.521	19.5
.727	19.0
.932	18.5
1.127	19.0
1.335	19.0
1.533	19.5
1.746	19.0
1.884	23.0
1.911	72.5
1.921	701.0
p	19.0
Benzidine, 25°	
0.101	5.5
.246	5.5
.388	5.7
.555	5.8
.786	5.7
1.075	5.8
1.274	6.0
1.579	6.0
1.790	8.5
1.860	34.0
1.905	78.0
1.918	734.0
p	6.0
Diethylaniline, 25°	
0.000	1.5
0.998	210.0
Evac.	8.0
n-Heptylamine in ether,[a] 20°	
0.000	8.0
.174	7.0
0.204	120.8
.410	249.0
.617	393.1
.803	529.5
1.010	679.5
Ethylaniline, 25°	
0.000	1.5
.182	46.5
.361	101.0
.536	172.5
.706	264.5
.870	378.0
1.027	510.0
1.183	655.0
Methylaniline, 25°	
0.000	2.0
.124	19.5
.258	42.0
.396	72.5
.525	114.4
.652	166.1
.772	237.0
.896	329.0
1.010	436.0
1.115	552.5
Dimethylaniline, 25°	
0.000	2.0
.185	14.6
.362	30.0
.564	56.5
.770	106.0
.950	189.1
1.090	290.2
1.271	449.5
1.400	575.0
n-Amylamine, 20°	
0.000	21.5
.108	78.5
.234	158.0
.359	177.0
.483	173.5
.561	8.5
.650	14.3
.769	23.1
.884	73.1
1.002	212.0
1.004	509.5
p	175.0 7.6
n-Amylamine in ether,[a] 20°	
0.000	13.0
.149	13.5
0.393	7.0
.594	8.0
.803	9.5
.918	46.0
.984	169.5
1.010	240.0
1.016	310.0
Evac.	9.0

[a] Experiments conducted in presence of dibutyl ether and results corrected for pressure and absorption by this solvent.

TABLE II

CONSTANTS FOR DIBUTYL ETHER

Solubility of SO_2 in 5 cc. at 20°		Const. of Henry	Vapor pressures at varying temperatures	
Mg. SO_2 adsorbed (W)	Press., mm. (P)	$K = P^1/W$, $P^1 = P - 11.0$	Temp., °C.	Press., mm.
0.0	11.0	..	11.3	7.5
76.4	87.5	1.00	15.4	9.0
154.1	170.5	1.04	19.7	10.5
229.1	250.1	1.05	25.0	12.5
312.8	332.4	1.03	25.9	12.7
396.0	413.5	1.02	29.7	14.5
476.2	483.5	0.99		

tion was 48.2 mm. In this case, as with the other two toluidines, the existence of compounds in the 1:1 ratio is indicated. The solid compounds are yellow, and the residual solution assumes an orange tint. For *m*-toluidine the invariant pressure is much higher, 323 mm. at 25°; it was necessary to undercool the solution in order to initiate crystallization. At 15° (curve 3, Fig. 1) the invariant pressures were determined by quantita-

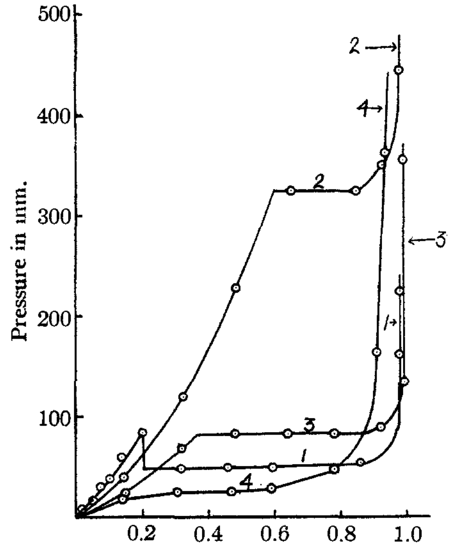

Fig. 1.—Toluidines with sulfur dioxide: curve 1, *o*-toluidine at 25°; curve 2, *m*-toluidine at 25°; curve 3, *m*-toluidine at 15°; curve 4, *p*-toluidine at 20°.

tive withdrawal of sulfur dioxide after use of an excess; the pressures thus obtained were much more nearly constant over most of the range. For the solid *p*-toluidine it was necessary to use the solvent; with the solid alone, equilibrium could not be approached within many centimeters over a period of several months. With the use of the solvent, the variation from constancy is much greater than can be assigned to the errors in the correction; at the first approach to constancy, however, the observed pressure (11 mm.) is in good agreement with the value (1.0 cm.) found by Foote and Fleischer[5] by another method.

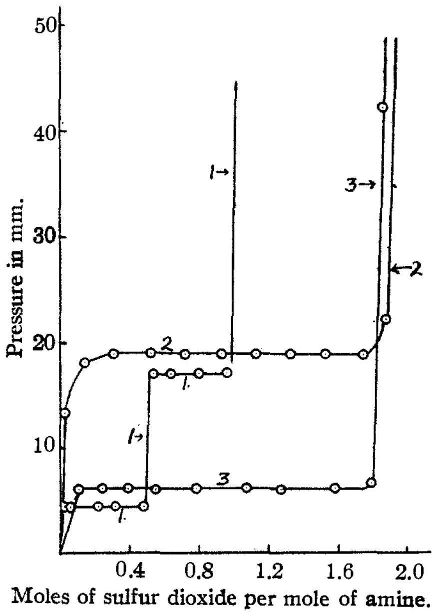

Fig. 2.—Phenylenediamines and benzidine with sulfur dioxide: curve 1, *o*-phenylenediamine at 25°; curve 2, *p*-phenylenediamine at 50°; curve 3, benzidine at 25°.

Quinoline, the Phenylenediamines and Benzidine.—The results with quinoline indicate (Fig. 5) the formation of a 1:1 compound, which was yellow in color. The very slow approach to equilibrium accounts for the distinct upward slope in the pressure curve for the invariant system; the pressure upon evacuation (45 mm.) is close to that of the beginning of the slope. Experiments with piperidine and with pyridine gave no solid compounds, but in the latter case there was marked absorption of gas and the formation of the typical orange-red solution which is characteristic for compound formation in this class. The two solid phenylenediamines could not be treated directly by successive addition of gas because of the slowness of reaction, nor in the presence of a solvent because of their insolubility. By treatment with an excess of sulfur dioxide and quantitative evacuation the results in Fig. 2 (curves 1 and 2) were obtained. The *o*-phenylenediamine reacts with sulfur dioxide in a 1:2 and a 1:1 ratio, giving red solids not distinguishable by the eye, but with clearly distinguishable pressures. The *p*-phenylenediamine (curve 2) also gives a red solid compound, but in an entirely unrelated ratio, 2:1. Benzidine, treated by the same method, gives also a 2:1 compound (curve 3) but of a yellow color not resembling the *p*-phenylenediamine analog. Comparison of these several compounds fails to indicate any simple relationship between the number of sulfur dioxide groups and the number of amino groups or phenyl groups, and makes it probable that any structural relationships must be sought in the field of secondary valence and not in any simple acid–base linkings.

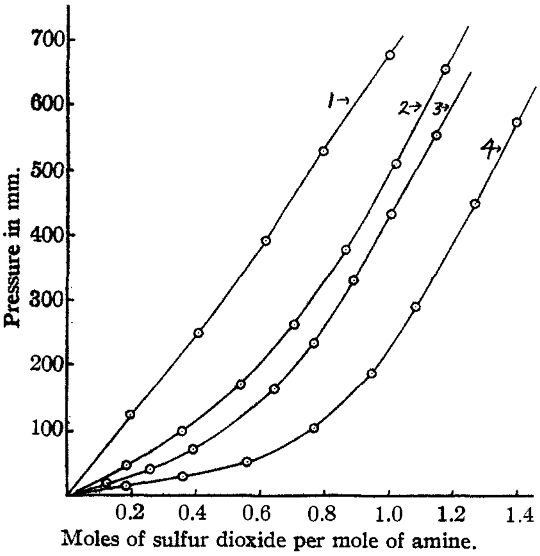

Fig. 3.—Homologs of aniline with sulfur dioxide at 25°: curve 1, diethylaniline; curve 2, ethylaniline; curve 3, methylaniline; curve 4, dimethylaniline.

Homologs of Aniline.—With the four homologs of aniline we obtained no solid phases, even upon cooling to −10° and seeding with the *o*-toluidine compound. Foote and Fleischer,[5] however, were successful in two of these cases (methylaniline and ethylaniline) in obtaining solid compounds; the melting points found were higher than the temperature of our experiments (25°) and show that our solutions were metastable in at least these two cases; the marked heat of absorption and the red color noted makes it seem probable to us that compound formation exists for all four cases. As will be seen in Fig. 3, there are positive deviations from Henry's law in all four cases, though the deviation is not great in the case of diethylaniline (curve 1).

Aliphatic Amines.—It has been shown previously by Michaelis[6] that sulfur dioxide gas reacts vigorously with aliphatic amines, pure or in ethereal solution, forming white compounds in the 1:1 ratio which lose sulfur dioxide in the air to become white compounds in the 1/2:1 ratio, as determined by analysis. With the lower aliphatic amines we were unable to secure quantitative results, as the pressures developed were erratic and not reproducible. With the amyl and heptyl amines, we were able to secure quantitative results but found that only the 1/2:1 compounds were white, the 1:1 compounds being yellow and resembling those of the aromatic series. With normal amylamine we obtained the unusual type of curve seen in Fig. 4; there is evidence of a metastable white compound showing the high pressure of about 175 mm. and presumably of the 1/2:1 ratio, and a stable yellow compound of low vapor pressure, 7.6 mm. The unusual behavior noted upon admission of gas to the system cannot be passed without comment; in the section a–b–c, admission of gas was followed by a rapid drop of pressure to a value *below* that of the pure amine (21.5 mm.) and the formation of a white deposit in the upper part of the vessel; the white solid gradually disappeared while the pressure slowly rose to the equilibrium value. Our interpretation is that there is very rapid reaction of sulfur dioxide with the amine in the gas phase to form a solid of low vapor tension, which, however, is very soluble in the liquid phase, so that saturation is not reached up to the point b; the curve a–b, therefore, represents the solubility of sulfur dioxide in the liquid, b–c represents as usual the pressure for the saturated solution plus white solid, while the curve of low pressure for the white solid into its gaseous products is not realizable. When the same *n*-amylamine was tested in dibutyl ether solution (Fig. 5, curve 1) the results were not in complete agreement with those of Fig. 4; a somewhat irregular pressure was found at about 14 mm. accompanied by the precipitation of a white compound, presumably the 1/2:1 compound; as the additions brought the composition up to about 0.5 mole of sulfur dioxide, the solid turned yellow and the corrected pressure upon partial evacuation was 8 mm., obviously that of the 1:1 compound. The *n*-butylamine behaved in the same fashion, giving a pressure upon evacuation of 9 mm. It is apparent that in these two cases the pressure for the 1/2:1 compound has not been realized.

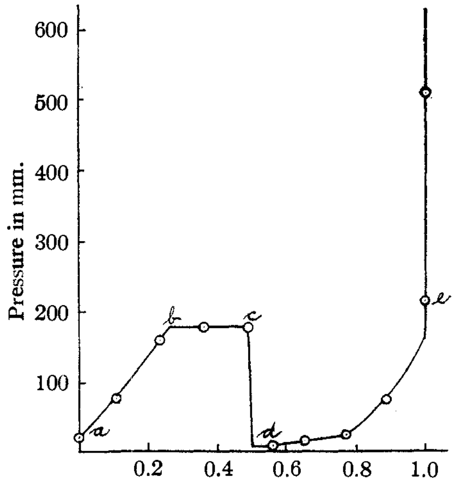

Fig. 4.—*n*-Amylamine and sulfur dioxide at 20°.

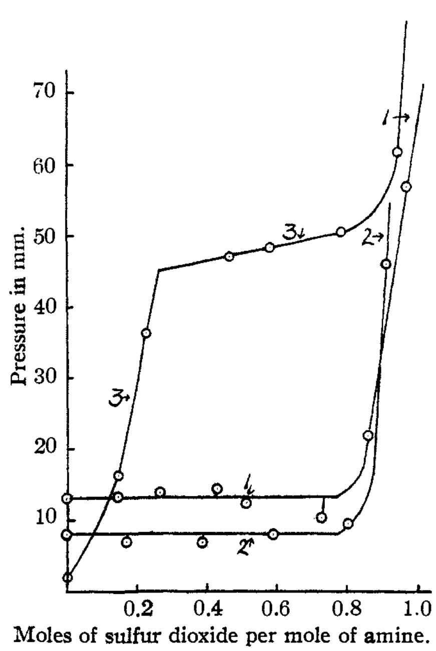

Fig. 5.—Curve 1, *n*-amylamine in butyl ether at 20°; curve 2, *n*-heptylamine in butyl ether at 20°; curve 3, quinoline and sulfur dioxide at 25° (without solvent).

Vapor Pressures and Heats of Formation.—The vapor pressures of six of the addition prod-

---

[6] Michaelis, *Ber.*, **24**, 745 (1891); *Ann.*, **274**, 192 and 208 (1892).

ucts have been measured at several temperatures and from them heats of formation have been calculated by substitution in the Clausius–Clapeyron formula. The measurements were made by the method of evacuation and are therefore subject to errors due to incomplete attainment of equilibrium. These errors are probably not greater than about 1 mm. at the lower pressures and 3 or 4 mm. at the higher pressures. The logarithms of the vapor pressures plotted against the reciprocals of the absolute temperatures gave reasonable concordance with straight lines. Vapor pressures calculated from the equations of these lines, in which the constants are so chosen as to give the pressure in millimeters, agree with the measured values within the experimental error.

TABLE III

VAPOR PRESSURES OF SULFUR DIOXIDE ADDITION PRODUCTS AT VARIOUS TEMPERATURES

Equation: $\log P = a - b(1/T \times 10^4)$

Compound	Temp. range, °C.	a	b	Heat of formation, cal.
o-Toluidine	10.8–50.4	16.529	0.4419	20,200
m-Toluidine	8.0–25.0	19.190	.4970	22,600
p-Toluidine	10.3–29.9	19.234	.5265	24,100
Quinoline	22.5–47.6	18.478	.5016	22,900
n-Amylamine	20.0–58.3	3.4481	.0771	3,500
n-Heptylamine	20.0–50.0	5.6392	.1391	6,400

For the three cases in which the use of dibutyl ether as solvent was necessary, namely, *p*-toluidine, *n*-amylamine and *n*-heptylamine, it is clear that the added corrections make the calculated heats of formation less accurate. It appears that 1:1 compounds of sulfur dioxide with the three toluidines and with quinoline have heats of formation of the same order as that found for the aniline compound,[4] which is 19,630 cal.; the two aliphatic amines give heats of reaction very markedly less (3500 cal. and 6400 cal.). It does not appear possible at this time to correlate the heats of formation or the vapor pressures of the compounds with their structures.

Summary

Compound formation has been studied between sulfur dioxide gas and a number of aromatic and aliphatic amines; the composition of these bodies, determined by phase-rule methods, shows variations in the ratio sulfur dioxide: amine from 1:2 to 2:1, the 1:1 ratio predominating. Vapor tension measurements of the systems have been made at different temperatures, and the approximate heats of formation calculated.

NEW YORK CITY RECEIVED SEPTEMBER 27, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

The Oxidation Potential of the Alkaline Permanganate–Manganese Dioxide Electrode

BY LYLE V. ANDREWS AND D. J. BROWN

No direct measurement of the potential of the alkaline permanganate–manganese dioxide electrode has been made. Inglis[1] measured the electrode in acid solution from which the value in alkaline solution was calculated to be 0.52 volt. Sackur and Traegner[2] measured the two electrodes MnO_4^-–$MnO_4^=$ in 1.5–5.8 *m* alkali and $MnO_4^=$–MnO_2 in 4–10 *m* alkali against Hg–HgO in 0.8 *m* alkali and calculated the value of the alkaline permanganate–manganese dioxide electrode to be 0.54 volt. Ruby[3] determined the equilibrium concentration for the reaction $3MnO_4^= + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$ and using Sackur and Traegner's value for the MnO_4^-–$MnO_4^=$ electrode, calculated the value of the alkaline permanganate–manganese dioxide electrode to be 0.647 volt. Schlesinger and Siems'[4] data for the reaction would give a slightly different value.

From the equilibrium relations for the reaction studied by Ruby and by Schlesinger and Siems, it is readily seen that the concentration of the manganate would decrease rapidly with dilution of the permanganate and hydroxide and in more diluted solutions the fraction of permanganate reduced by the manganese dioxide would be less than the experimental error in its effect on any observed potential. We believe more accurate values should be obtained in more diluted solutions than those previously used. A study from this point of view is presented in this paper.

---

[1] Inglis, *Z. Elektrochem.*, **9**, 226 (1903).

[2] Sackur and Traegner, *ibid.*, **18**, 718 (1912).

[3] Ruby, THIS JOURNAL, **43**, 294 (1921).

[4] Schlesinger and Siems, *ibid.*, **46**, 1965 (1924).