

CXLI.—*The Reactivity of Antimony Haloids with Certain Aromatic Compounds. Part I.*

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In a recent paper (T., 1913, 103, 1826) the thermal diagrams of some binary systems of the types Ph. α . α .Ph and Ph. α . β .Ph were described.

In the fifteen compounds chosen for investigation, α and β represented the following atoms and groups: CH₂, :CH, C:, CO, CH(OH), O, CS, N, NH; with the exception of the first, each possesses residual affinity, and each compound (except *s*-diphenylethane) is an example of a compound containing conjugated linkings, in which the residual affinity of the unsaturated atoms or groups, α and β , is conjugated with that of the phenyl groups.

An investigation of the co-ordinative compounds which these substances form with antimony haloids would consequently be likely to yield interesting results, and might show the effect of the conjugation of the residual affinity on the reactivity of the phenyl group.

It is, in fact, a method of treating the problem of the relationship between residual affinity and chemical constitution.

Since 1903, B. N. Menshutkin has investigated a large number of mixtures of the haloids of calcium, magnesium, aluminium, and antimony with organic compounds, but in no case have the investigations included compounds of the type mentioned above.

I communicated with Professor Menshutkin, and he readily assented to my undertaking the work.

The present paper deals with the investigation (by the method of thermal analysis) of the eight systems obtained from antimony trichloride and tribromide, and the four symmetrical compounds: *s*-diphenylethane, CH₂Ph·CH₂Ph; stilbene, CHPh:CHPh; azobenzene, NPh:NPh; and benzil, CPh·CPh.

EXPERIMENTAL.

The System: Antimony Trichloride-s-Diphenylethane.

The freezing points of mixtures of these two substances were determined in the manner described in former papers (*loc. cit.*). The temperatures found have been plotted as ordinates against molecular percentages as abscissæ in the diagram below (Fig. 1).

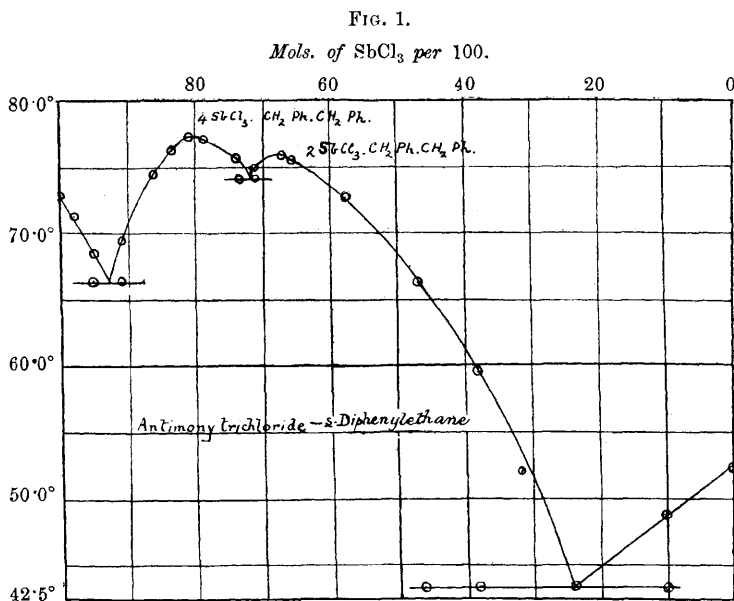
The temperatures and concentrations are given in table I. The diagram consists of four branches, showing the existence of two stable compounds having the compositions 4SbCl₃.C₁₄H₁₄ and

$2\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$. The former melts at 77.5° , and the latter at 76.0° ; both these temperatures are above the melting points of the constituents. The diagram also shows two eutectic points at concentrations represented by 93.4 and 24 per cent. of antimony trichloride, and temperatures 66.4° and 43.3° respectively.

It is seen, also, that the compound $4\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$ undergoes transformation into $2\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$ at a concentration of 72 per cent. of antimony trichloride and 74.2° .

The System: Antimony Tribromide-s-Diphenylethane.

The thermal diagram (Fig. 2) obtained for this system consists of three branches, showing the formation of one stable compound



having the composition $4\text{SbBr}_3, \text{C}_{14}\text{H}_{14}$, which melts at 87° , 8° below the melting point of the tribromide.

Eutectic points were found at concentrations 89 and 27 per cent. of antimony tribromide, and temperatures 84.3° and 42.8° respectively.

Only one type of compound is formed in this system, so that s -diphenylethane combines less readily with the tribromide than with the trichloride.

The temperatures and concentrations for the various mixtures are given in table II.

FIG. 2.

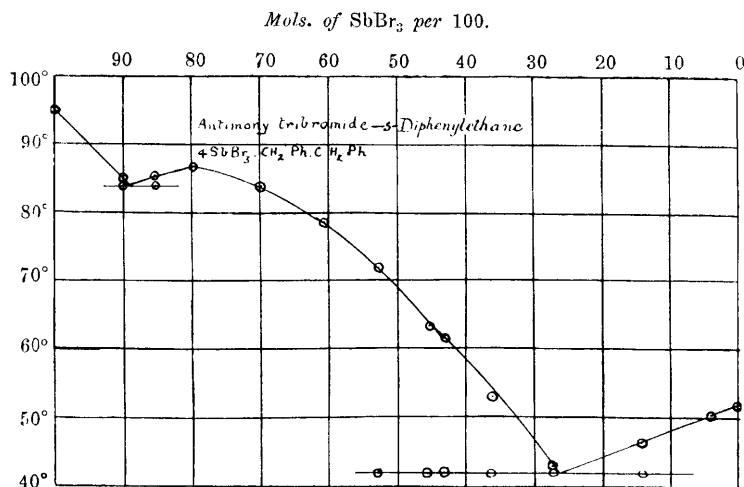


TABLE I.

Mols. of SbCl ₃ per 100.	<i>t</i> ₁ .	<i>t</i> ₂ .
100.0	73.0°	—
98.14	71.2	—
95.03	68.1	66.4°
91.10	69.4	66.4
86.11	74.6	66.4
83.60	76.5	—
80.96	77.3	—
78.71	77.2	—
74.00	75.9	74.2
73.83	74.2	—
71.25	74.7	74.2
67.01	76.0	—
65.90	75.6	—
57.45	72.9	—
53.70	71.4	—
47.12	66.4	43.3
38.29	59.7	43.3
32.10	51.8	43.3
23.85	43.3	43.3
9.66	48.9	43.3
0.0	51.5	—

In the above table, and in those that follow, *t*₁ represents the first freezing point and *t*₂ the temperature at which solidification is complete.

TABLE II

Mols. of SbBr ₃ per 100.	<i>t</i> ₁ .	<i>t</i> ₂ .
100.0	94.9°	—
89.74	85.1	84.3°
85.00	85.6	84.3
78.84	87.1	—
70.00	84.3	—
60.42	79.0	—
52.58	72.2	42.8
44.88	63.3	42.8
43.09	61.8	42.8
36.10	53.0	42.8
27.00	43.2	42.8
13.96	46.6	42.8
3.74	50.5	—
0.0	51.5	—

The Influence of the Number and Position of Phenyl Groups on the Reactivity of Hydrocarbons with Antimony Haloids.

A comparison of the above systems with those of other hydrocarbons hitherto investigated by Menshutkin (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1805) leads to interesting results. It will be seen from table III below, comparing the systems with benzene, *s*-diphenylethane, and triphenylmethane, having one, two, and three phenyl groups respectively, that increasing the number of phenyl groups diminishes the reactivity or capacity to combine with antimony haloids thus: benzene forms the compounds 2SbCl₃.C₆H₆ and 2SbBr₃.C₆H₆, both being stable; diphenyl also combines with 2SbCl₃ and 2SbBr₃, but the compound with the tribromide is unstable; with triphenylmethane, the compound with antimony trichloride is unstable, and no combination takes place with the tribromide.

Comparing, now, diphenyl, diphenylmethane, and *s*-diphenylethane, it is found that the influence of the second phenyl group, in diminishing the reactivity, is decreased the further it is removed from the first; thus, as already stated, diphenyl forms a stable compound with 2SbCl₃, but the compound with 2SbBr₃ is unstable, whereas with diphenylmethane both compounds are stable, and, lastly, with *s*-diphenylethane the influence of the second phenyl group has almost disappeared, since it is capable of combining with four molecular proportions of the antimony haloids to form stable compounds.

That the influence of the second phenyl group has not entirely disappeared can be seen by comparing its reactivity towards antimony haloids with that of toluene.

Toluene forms two stable compounds, both with the trichloride and the tribromide, of the type 2SbX₃.C₇H₈ and SbX₃.C₇H₈,

s-diphenylethane forms two stable compounds with the trichloride having the formulæ $4\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$ and $2\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$, thus behaving as if it were composed of two molecules of toluene; but it is only capable of forming one compound with antimony tribromide, namely, $4\text{SbBr}_3, \text{C}_{14}\text{H}_{14}$, whereas toluene forms two compounds.

TABLE III.

Hydrocarbon.	Compounds with SbCl_3 .	Nature.	Compounds with SbBr_3 .	Nature.
Benzene	$2\text{SbCl}_3, \text{C}_6\text{H}_6$	Stable	$2\text{SbBr}_3, \text{C}_6\text{H}_6$	Stable
Toluene	$2\text{SbCl}_3, \text{C}_7\text{H}_8$	Stable	$2\text{SbBr}_3, \text{C}_7\text{H}_8$	Stable
	$\text{SbCl}_3, \text{C}_7\text{H}_8$	Stable	$\text{SbBr}_3, \text{C}_7\text{H}_8$	Stable
Diphenyl	$2\text{SbCl}_3, \text{C}_{12}\text{H}_{10}$	Stable	$2\text{SbBr}_3, \text{C}_{12}\text{H}_{10}$	Unstable
Triphenylmethane	$2\text{SbCl}_3, \text{C}_{12}\text{H}_{16}$	Unstable	None	
Diphenylmethane .	$2\text{SbCl}_3, \text{C}_{13}\text{H}_{12}$	Stable	$2\text{SbBr}_3, \text{C}_{13}\text{H}_{12}$	Stable
<i>s</i> -Diphenylethane .	$4\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$	Stable	$4\text{SbBr}_3, \text{C}_{14}\text{H}_{14}$	Stable
	$2\text{SbCl}_3, \text{C}_{14}\text{H}_{14}$	Stable	—	

It is seen from the above that the series benzene, diphenyl, triphenylmethane are in decreasing order of reactivity towards antimony haloids, whilst the series diphenyl, diphenylmethane, *s*-diphenylethane are in increasing order of reactivity.

This is in agreement with the results of the examination of the optical properties (Perkin, T., 1895, **69**, 1152; Smedley, T., 1908, **93**, 372; 1909, **95**, 230; 1910, **97**, 1475).

The molecular refractive power is exalted when the number of phenyl groups is increased, but the exaltation falls when the phenyl groups are separated. It is to be observed that *s*-diphenylethane has practically the normal value for the molecular refractive power. The values are given in the table below.

TABLE IV.

Hydrocarbon.	M_d observed.	M_d calculated.	Difference
Benzene	25.93	26.31	-0.38
Toluene	30.79	30.89	-0.10
Diphenyl	51.93	50.42	+0.51
Triphenylmethane	79.57	79.11	+0.46
Diphenylmethane	55.13	55.00	+0.13
<i>s</i> -Diphenylethane	59.60	59.64	-0.04

The System: Antimony Trichloride-Stilbene.

This system, and the others that follow, proved far more difficult to investigate than those with *s*-diphenylethane. It was found that stilbene combined with two molecular proportions of antimony trichloride, but the compound was very difficult to obtain. The fused mixtures could be supercooled greatly, and many of them were viscous liquids at room temperature, crystallising with extreme slowness on seeding with some of the compound. The freezing points given in table V were obtained by fusing the freshly-made

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mixtures and cooling rapidly in the air. The diagram (Fig. 3) shows that the compound has the composition $2\text{SbCl}_3 \cdot \text{C}_{14}\text{H}_{12}$; the substance melts at 98° .

Eutectic points are shown at concentrations 80 and 55 per cent. of antimony trichloride, and temperatures 47° and 75.5° respectively. It is concluded that stilbene only enters into feeble union with antimony trichloride, and that it is possible to obtain a diagram consisting of two branches only, intersecting in a eutectic point at a low temperature, and showing no chemical combination.

FIG. 3.

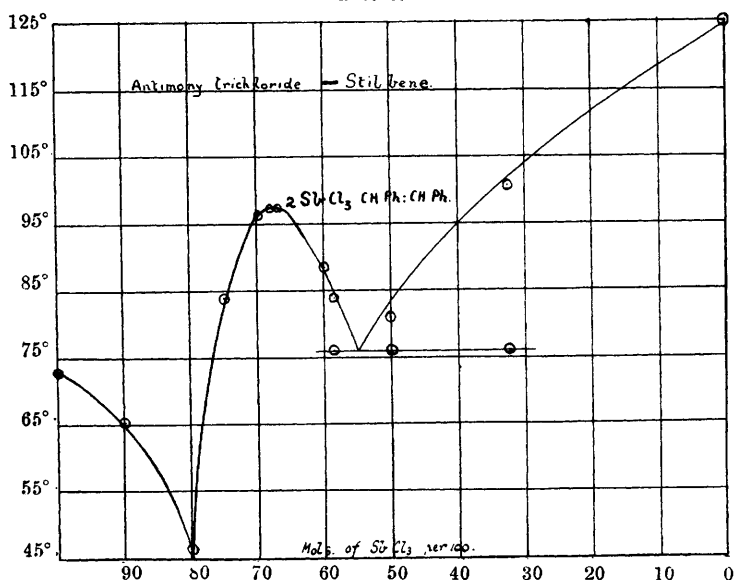


TABLE V.

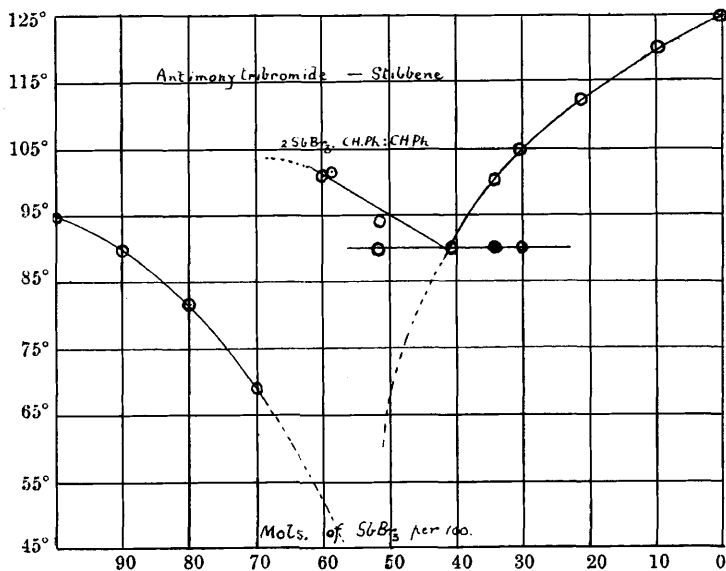
Mols. of SbCl_3 per 100.	t_1 .	Remarks.
100.0	73.0°	—
90.0	65.2	Seeded with SbCl_3
80.0	46.4	Seeded with SbCl_3
70.0	—	Cooled to 15° without solidification
70.0	93.4	Rapidly cooled in air; solid used for seeding
70.0	96.3	Cooled in air and seeded
75.0	83.8	—
67.98	97.3	—
66.6	97.3	—
60.00	88.5	—
58.58	83.8	Complete at 75°
50.00	80.7	Second f. p. at 75.5°
32.46	100.5	Second f. p. at 76°
0.0	125.0	—

The System: Antimony Tribromide-Stilbene.

This system presented the same difficulties as the preceding. Mixtures containing excess of stilbene solidified readily. At a concentration of 41 per cent of antimony tribromide the eutectic point on the right-hand side of the diagram (Fig. 4) was reached; the temperature corresponding was 90° .

On increasing the amount of antimony tribromide, the freezing points rose. The mixtures containing 50 and 60 per cent. of antimony tribromide gave freezing points on cooling rapidly in air

FIG. 4.



at 94° and 101° respectively. Other mixtures containing excess of antimony tribromide, namely, 30, 20, and 10 per cent., only gave freezing points when inoculated with antimony tribromide. The diagram (Fig. 4) thus shows that a compound is formed in the presence of excess of stilbene, but the maximum point was not obtained. There is again a tendency to give a diagram showing a single eutectic point at a low temperature. It is probable that the unstable compound has the composition $2\text{SbCl}_3 \cdot \text{C}_{14}\text{H}_{12}$.

The temperatures and concentrations are given in table VI.

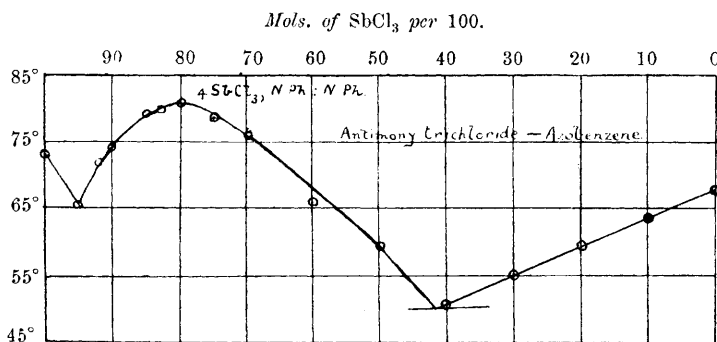
TABLE VI.

Mols. of SbBr ₃ per 100.	<i>t_f</i> .	Remarks.
100.0	94.9°	—
90.03	89.5	—
80.00	81.7	—
79.20	81.0	—
70.03	69.0	—
70.00	62.0	Slow crystallisation seeded with SbBr ₃
60.00	101	—
58.40	102	—
51.18	94.3	Second f. p. at 90°
40.69	90.0	Complete solidification
34.02	100.0	—
30.28	104.5	—
21.36	112.0	—
10.04	120.0	—
0.0	125.0	—

The System: Antimony Trichloride—Azobenzene.

The freezing points of mixtures of these two substances were readily obtained, provided the fusions were seeded with the correct

FIG. 5.



phase. The diagram (Fig. 5) shows the existence of a stable compound having the composition $4\text{SbCl}_3 \cdot \text{C}_{12}\text{H}_{10}\text{N}_2$. It consists of three branches; the middle branch shows the existence of a stable compound having the composition $4\text{SbCl}_3 \cdot \text{C}_{12}\text{H}_{10}\text{N}_2$, and melting at 81° .

This portion of the diagram, however, could not be obtained unless the corresponding mixtures were seeded with some of the compound previously prepared.

Eutectic points occur at concentrations 95 and 44 per cent. of antimony trichloride, and temperatures 66° and 50.5° respectively. The concentrations and corresponding temperatures are given in table VII.

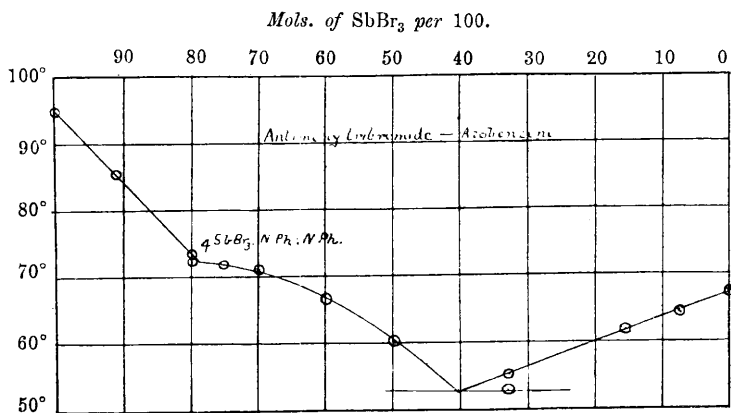
TABLE VII.

Mols. of SbCl_3 per 100.	t_1	t_2
100.0	73.0°	—
95.00	65.6	—
92.00	71.8	—
89.93	74.2	—
85.00	79.5	—
83.63	80.0	—
80.00	80.7	—
75.01	78.3	—
69.67	76.1	—
59.97	65.4	—
50.16	59.2	—
40.09	50.5	50.5
29.93	54.8	—
19.94	59.2	—
9.98	63.1	—
0.0	68.0	—

The System: Antimony Tribromide—Azobenzene.

This system presented no great difficulty after the experience gained with the preceding. The compound separated out readily

FIG. 6.



on seeding with a little of the previously prepared substance. Table VIII shows the concentrations and temperatures of solidification. The thermal diagram (Fig. 6) is of special interest. It consists of three branches, but the middle portion does not show a maximum point. The compound decomposes before its melting point is reached.

A mixture containing 80.0 per cent. of antimony tribromide showed a longer arrest at the eutectic point, 72.5°, than a mixture

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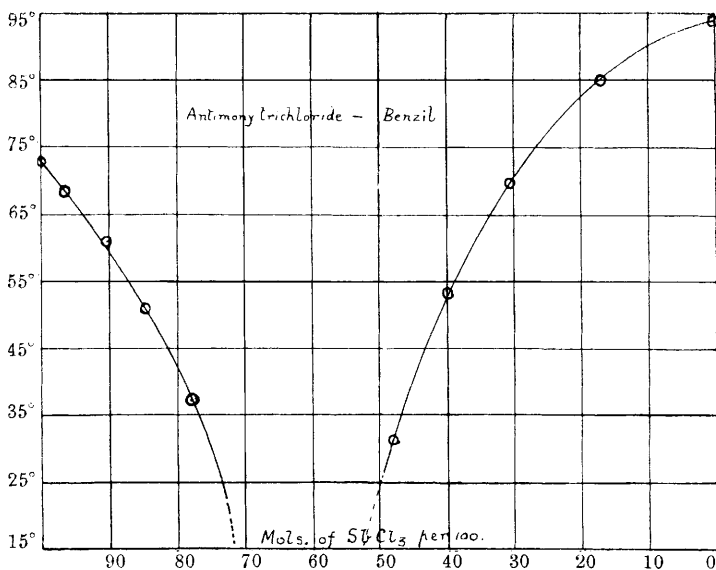
containing 75 per cent. of antimony tribromide, so that the composition of the compound is known to be $4\text{SbBr}_3\cdot\text{C}_{12}\text{H}_{10}\text{N}_2$.

Eutectic points occur at temperatures 72.5° and 52.7° , and concentrations 77.5 and 40.5 per cent. of antimony tribromide respectively.

TABLE VIII.

Mols. SbBr_3 per 100.	t_1 .	Remarks.
100.0	95.0°	
91.08	85.6	
80.00	73.4	Seeded with SbBr_3
—	72.4	Seeded with compound; complete solidification
75.00	72.2	
70.00	71.2	
60.00	66.7	
50.00	60.2	
42.69	52.9	
32.79	55.4	Second f. p. at 52.8°
15.66	61.9	
7.39	64.2	
0.0	68.0	

FIG. 7.

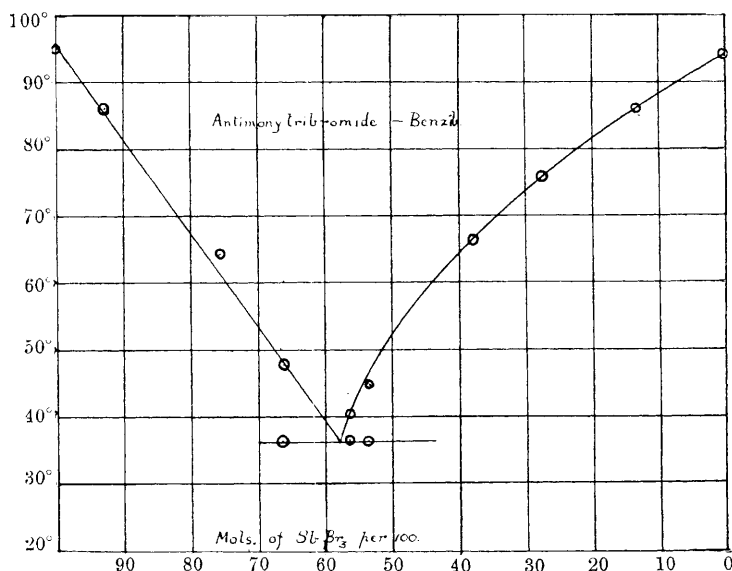


The Systems: Antimony Trichloride-Benzil and Antimony Tribromide-Benzil.

The thermal diagrams (Figs. 7 and 8) obtained for these systems show that benzil has no capacity for combination with antimony haloids. Each diagram consists of two branches, meeting in a eutectic point.

The slope of the curves for the system antimony trichloride-benzil is very steep, and the eutectic temperature is consequently very low. It was not found possible to determine this temperature. The mixture containing 40 per cent. of antimony trichloride could be enormously supercooled. At the temperature of solid carbon dioxide and ether it formed a hard, vitreous mass, but did not crystallise; it behaved similarly on cooling in liquid air.

FIG. 8.



The eutectic temperature for the system antimony tribromide-benzil is at 36° , the concentration being 58.5 per cent. of antimony tribromide.

The temperatures and concentrations for these systems are given in tables IX and X.

TABLE IX.

Mols. of $SbCl_3$ per 100.	t_1 .
100.0	73.0°
96.45	68.5
90.47	61.0
84.62	51.0
78.24	37.0
70.00 *	
40.00	54.0
48.26	31.0
30.59	69.4
16.81	84.0
0.0	94.0

* This mixture—70.0 per cent.—did not solidify in liquid air.

TABLE X.

Mols. of SbBr ₃ per 100.	<i>t</i> ₁ .	<i>t</i> ₂ .
100.0	95.0°	—
93.10	86.1	—
75.59	64.6	—
66.35	48.0	36.2°
55.89	41.6	—
53.35	44.1	—
37.77	66.3	—
27.40	76.0	—
13.28	86.1	—
0.0	94.0	—

Discussion of Results.

The systems described above show quite clearly that with compounds containing conjugated linkings the reactivity towards antimony haloids is greatly diminished. The effect of the conjugation appears to be greatest with benzil, the compound containing two carbonyl groups conjugated with the phenyl groups, since it does not show any capacity to combine with antimony trichloride and tribromide.

Next in order comes stilbene, which contains an ethenoid linking conjugated with the phenyl groups. It is only capable of combining with two molecules of the antimony haloids, and the compounds formed are unstable.

With azobenzene, the influence of conjugation is plainly evident, but the reactivity is not diminished to so great an extent as with stilbene and benzil. It is capable of combining with four molecules of antimony trichloride and tribromide, but with the latter the compound decomposes before the melting point is reached.

With *s*-diphenylethane there is no conjugation outside the phenyl groups, and the reactivity is very great, two compounds being formed with the trichloride and one with the tribromide, all three being stable.

The compounds and melting points are tabulated below.

Compound.	Nature.	Melting Point.
4SbCl ₃ , C ₁₄ H ₁₄	Stable	77.5°
2SbCl ₃ , C ₁₄ H ₁₄	"	76.0
4SbBr ₃ , C ₁₄ H ₁₄	"	87.0
4SbCl ₃ , C ₁₂ H ₁₀ N ₂	"	81.0
4SbBr ₃ , C ₁₂ H ₁₀ N ₂	Decomposes	72.4
2SbCl ₃ , C ₁₄ H ₁₂	Unstable	98.0
2SbBr ₃ , C ₁₄ H ₁₂	"	Not reached.

It is of interest to compare the optical properties of the substances *s*-diphenylethane, stilbene, azobenzene, and benzil in order to see how far they agree with the results of the present work. The molecular refractive powers of these substances have been

determined by different observers, using different solvents, so that the values given in the table below are not strictly comparable :

Compound.	M_a observed.	M_a calculated.	Δ
<i>s</i> -Diphenylethane	59.60	59.64	-0.04
Azobenzene	63.91	58.42	5.49
Stilbene	65.65	59.20	6.45
Benzil	63.48	61.33	2.14

It will be noticed that the optical exaltation for stilbene is very large, and greater than that for azobenzene. This is in agreement with its smaller reactivity with antimony haloids.

The lower exaltation of benzil has been discussed by Smedley (*loc. cit.*). The proximity of the oxygen atoms in the contiguous carbonyl groups probably lowers the exaltation. There is some evidence, also, that the substance can oscillate between the diketonic and peroxidic constitution.

s-Diphenylethane is optically normal, and this is in agreement with its great reactivity with antimony haloids.

The effect of increasing the number of carbonyl groups can be seen by comparing diphenyl, benzophenone, and benzil :

	Compound with $SbCl_3$.	Compound with $SbBr_3$.	Exaltation.
Diphenyl	$2SbCl_3 \cdot C_{12}H_{10}$	$2SbBr_3 \cdot C_{12}H_{10}$	+0.51
Benzophenone ...	$SbCl_3 \cdot C_{13}H_{10}O$	$SbBr_3 \cdot C_{13}H_{10}O$	+0.98
Benzil	No compound	No compound	+2.14

The introduction of one carbonyl group between the phenyl groups in diphenyl lowers its reactivity with antimony haloids by one-half, since diphenyl combines with two molecules of the haloids and benzophenone with only one. It is seen that the exaltation of molecular refractive power for benzophenone is double that for diphenyl.

When a second carbonyl group is introduced, as in benzil, the exaltation is again doubled, and the reactivity with antimony haloids has practically vanished.

The investigation by thermal analysis of systems with antimony haloids thus provides a useful method of tracing the conjugation of the residual affinity of the unsaturated atoms and groups CH^{\cdot} , N^{\cdot} , CO with the phenyl groups in compounds of the type $Ph.\alpha.\alpha.Ph$.

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