

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

THERMAL ENERGY STUDIES. II. PHENYL DERIVATIVES OF METALS¹

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In planning the study of thermal energy in phenyl derivatives as outlined in the previous paper of this series,² it seemed desirable to include some compounds which would introduce other variables than those found in the purely organic molecules. Of the many compounds available, the phenyl derivatives of the metals are almost ideally fitted for this purpose because a change in the central metal atom presumably brings about a change in the size of the molecule and in the separation of the phenyl groups, as well as a change in the valence force. Accordingly there were obtained fourteen phenyl derivatives of various metals and elements closely related to them and the specific heats were measured by the method described in the first paper of this series.

Preparation of Materials

The same general procedure for preparation and purification was followed as described in the first paper of this series.² The meaning of the symbols used below may be found in that paper.²

Triphenylamine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 126.5°; T. C., 125.8°; I. C. T., 126.5°; T. T. C., 0.2% (impurities estimated from time-temperature curves).

Triphenylphosphine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 77-77.5°; T. C., 74.7°; I. C. T., 79°; T. T. C., 2%. This value is doubtful because the temperature does not rise to the melting point when the compound freezes. The triphenyl compounds of the elements of the fifth group apparently have quite low heats of fusion.

Triphenylarsine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 59-59.3°; T. C., 56.4°; I. C. T., 60°; T. T. C., 1% (see triphenylphosphine).

Triphenylstibine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 51.5-52.5°; T. C., 48.0°; I. C. T., 48°; T. T. C., 1.5% (see triphenylphosphine).

Triphenylbismuthine.—This compound was prepared at the University of Illinois and was used as received.—m. p.: M. T., 76.5-77.5°; T. C., 73.5°; I. C. T., 78°; T. T. C., 2.0% (see triphenylphosphine).

Mercury Diphenyl.—Dr. Parry Borgstrom, of the Naval Research Laboratory, Washington, D. C., prepared this compound and it was used as received.—m. p.: M. T., 124-125°; S. (1912-1913), 121.8°; S. (1916-1918), 120-123°. (S. refers to Stelzner's, "Literatur Register der organische Chemie.")

¹ From the dissertation submitted by R. H. Smith to the Faculty of Philosophy The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Richard H. Smith and Donald H. Andrews, *THIS JOURNAL*, 53, 3644 (1931).

Mercury Di-(*p*-tolyl).—The Eastman Kodak Company preparation was used as received.—m. p.: M. T., 238–239°; B., 232–233°.

Tetraphenylsilicane.³—This was prepared by treating bromobenzene and silicon tetrachloride in ether solution with sodium. It was three times recrystallized from benzene.—m. p.: M. T., 233–235°; S. (1912–1913), 233°.

Tetraphenyl Tin.—This compound was prepared by Dr. Parry Borgstrom and was used as received.—m. p.: M. T., 225.5–226.5°; S. (1919–1921), 226°.

Diphenyl oxide supplied by the Dow Chemical Works was fractionated through the column.—b. p. 83–84° at 1 mm.; m. p.: M. T., 26.6–26.9°; T. C., 26.75°; I. C. T., 26.9°; T. T. C., 0.5%.

Diphenyl Sulfide.—The Eastman Kodak Company preparation was used as received.—m. p.: M. T., –25.9°; T. T. C., 2.5%.

Diphenyl Sulfoxide.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 68–70°; T. C., 69.4°; I. C. T., 70.5°; T. T. C., 0.8%.

Diphenyl Sulfone.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 128–128.5°; T. C., 127.2°; I. C. T., 129°; T. T. C., 1.0%.

Results

The data for the different compounds are presented in Tables I, II, III and IV and in Figs. 1 and 2. The curves are of the same general type as those of purely organic molecules and there does not appear to be any unusual heat of transition or other thermal phenomenon. It may readily be seen, however, that the nature of the central metal atom has a decided effect on the heat capacity. This is particularly noticeable in the

TABLE I

MOLAL HEAT CAPACITIES OF PHENYL AND TOLYL SUBSTITUTED MERCURY

T, °K.	Mercury	
	diphenyl Calories per degree	Mercury di- <i>p</i> -tolyl Calories per degree
101.9	23.8	30.5
126.1	27.2	34.9
147.4	30.1	38.4
166.7	32.8	41.7
184.4	35.5	44.3
201.1	38.3	47.4
216.8	40.9	50.0
231.7	43.2	52.3
246.0	45.4	54.6
259.8	47.3	56.3
273.1	49.5	58.2
286.0	51.7	60.2
298.5	53.9	62.7
310.7	56.1	65.5
322.6	58.2	67.7
334.3	60.4	70.1
345.7	62.4	71.9

TABLE II

MOLAL HEAT CAPACITIES OF THE TETRAPHENYL COMPOUNDS OF ELEMENTS IN THE FOURTH GROUP OF THE PERIODIC TABLE

T, °K.	Tetra-phenyl- methane —Calories per degree—		
	Tetra-phenyl- methane	Tetra-phenyl- silicane	Tetra-phenyl tin
101.9	33.9	41.8	42.0
126.1	39.4	47.6	49.1
147.4	44.7	53.3	55.3
166.7	49.6	58.6	60.7
184.4	54.7	62.8	65.9
201.1	59.1	68.2	71.0
216.8	63.0	73.7	75.6
231.8	67.7	77.0	79.8
246.0	71.4	81.1	84.6
259.8	75.4	83.4	89.1
273.1	79.9	87.0	93.4
286.0	84.0	90.3	97.4
298.5	88.0	94.6	101.9
310.7	92.2	101.0	106.3
322.6	96.4	105.4	110.0
334.3	100.2	110.5	113.4
345.7	103.8	114.1	116.2

³ Polis, *Ber.*, 18, 1542 (1885); Kipping and Lloyd, *J. Chem. Soc.*, 79, 451 (1901).

TABLE III
MOLAL HEAT CAPACITIES OF THE TRIPHENYL COMPOUNDS OF ELEMENTS IN THE FIFTH
GROUP OF THE PERIODIC TABLE

T, °K.	Triphenyl- amine	Triphenyl- phosphine	Triphenyl- arsine	Triphenyl- stibine	Triphenyl- bismuthine
	Calories per degree				
101.9	27.1	28.4	30.5	35.3	35.3
126.1	31.8	33.3	35.8	39.6	40.2
147.4	36.3	37.6	40.3	44.5	44.8
166.7	40.1	41.2	44.5	48.6	49.3
184.4	44.1	45.0	48.5	52.3	52.6
201.1	48.0	48.4	52.2	56.3	56.8
216.8	51.5	52.0	56.2	61.1	60.9
231.7	55.0	55.8	59.8	63.8	64.2
246.0	58.2	60.1	63.2	66.7	67.2
259.8	61.4	64.1	70.9	73.4	75.1
273.1	64.6	67.6	69.6	70.5	72.1
286.0	67.9	70.9	72.9	73.4	75.1
298.5	71.1	74.7	76.8	77.8	78.5
310.7	74.1		80.7	83.3	82.3
322.6	77.1				85.0
334.3	79.8				
345.7	82.2				

TABLE IV
MOLAL HEAT CAPACITIES OF DIPHENYL OXIDE, DIPHENYL SULFIDE AND THE OXIDATION
PRODUCTS OF DIPHENYL SULFIDE

T, °K.	Diphenyl oxide	Diphenyl sulfide	Diphenyl sulfoxide	Diphenyl sulfone
	Calories per degree			
101.9	20.3	22.3	23.3	24.1
126.1	23.6	26.0	27.3	28.1
147.4	26.5	29.5	30.7	31.7
166.7	29.3	32.7	33.6	34.6
184.4	31.9	35.8	36.6	38.0
201.1	34.8	..	39.6	40.9
216.8	37.4	..	42.4	44.0
231.7	39.8	..	45.1	46.5
246.0	42.2	Liquid	47.6	49.1
259.8	44.3	61.5	50.3	51.6
273.1	46.8	62.3	52.5	53.8
286.0	49.0	63.5	54.7	56.0
298.5	51.6	64.8	57.3	58.4
310.7			60.0	60.8
322.6			62.7	62.9
334.3				64.9
345.7				66.7

series containing elements from the fifth group of the periodic table. The tendency is for the heat capacity to increase with increasing atomic weight, but in proceeding from the amine to the phosphine, or from the stibine to the bismuthine, the additional weight does not appear to have any effect.

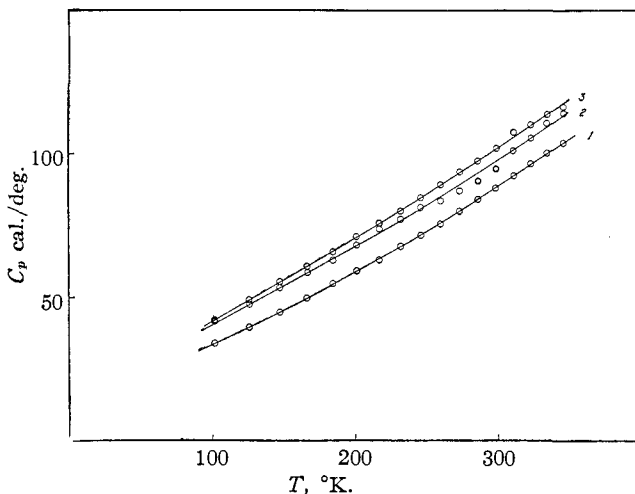


Fig. 1.—Molal heat capacities of the tetraphenyl compounds of elements in the fourth group of the periodic table: 1, tetraphenylmethane; 2, tetraphenylsilicane; 3, tetraphenyl tin.

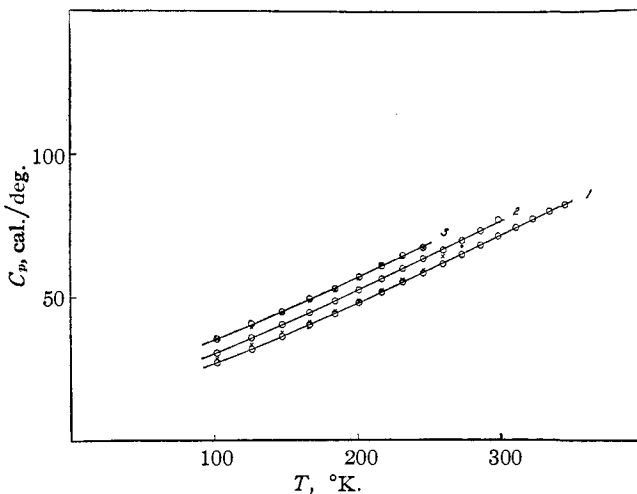


Fig. 2.—Molal heat capacities of the triphenyl compounds of elements in the fifth group of the periodic table: 1, triphenylamine—the X's along this curve are for triphenylphosphine; 2, triphenylarsine; 3, triphenylbismuthine—the X's are for triphenylstibine.

There are three ways in which one might expect the heat capacity to be affected by the change in the central atom. In the first place, an increase in weight would lower the frequency of vibration, which in turn would increase the heat capacity since the vibration is definitely quantized for

nearly all the motions which primarily involve the central atom. In the second place, changing the central atom may mean an increase in the volume of the molecule which in turn may result in greater freedom of motion of the phenyl groups, and consequent increase in heat capacity. Thirdly, changing the central atom may mean a change in the strength of the bonds which tie the phenyl groups to the central atom, and this might well vary the heat capacity throughout the entire molecule.

In order to observe more clearly the evidence for these effects, a table has been prepared which presents that part of the heat capacity of each molecule which remains when the heat capacities of the phenyl groups have been subtracted. As may be seen in the previous paper,² the addition of a phenyl group adds the same amount to the heat capacity of the molecule, in nearly all cases. Averaging the increments found in the study of the hydrocarbons, we can take this value, multiply it by the numbers of phenyl groups present, and subtract the result from the observed heat capacity at any given temperature. This gives us a value which represents roughly the part of the heat capacity due to the central atom and to the motion of the molecule as a whole in the crystal lattice. Calculations of this sort have been made for three temperatures and the results are given in Table V.

TABLE V
CALCULATED COMPARATIVE DATA

Central atom	At. wt.	θ	C_p , calculated for central atom			C_p , excess over phenyl groups		
			126.1°K.	216.8°K.	322.6°K.	126.1°K.	216.8°K.	322.6°K.
C	12	1560	0.0	0.2	1.1	8.6	12.6	14.8
Si	28	1030	0.1	1.2	2.7	16.8	23.3	23.8
Sn	119	500	1.8	3.9	5.0	18.3	25.2	28.4
N	14	1450	0.0	0.4	1.4	8.7	13.7	14.9
P	31	970	0.2	1.5	3.0	10.2	14.2	..
As	74	620	1.1	3.2	4.4	12.7	18.4	..
Sb	120	490	1.9	4.0	5.0	16.5	23.3	..
Bi	208	370	3.0	4.7	5.4	17.1	23.1	23.8

In order to get an idea of the change in heat capacity due to the increase in weight, another series of calculations has been made. Our molecule is made up of the central metal atom surrounded in space by the phenyl groups attached to it. In the case of three- or four-valent metals the principal forces which restrain the motion of the central atom will be the homopolar bonds which link it to the phenyl groups. As a first approximation we may regard the resultant of these forces as producing a restoring force which will be practically the same for any direction of motion of the central atom. The movements at the central atom will therefore approximate harmonic vibrations in the three directions in space and will have a single common frequency.

In order to ascertain the effect of weight as distinguished from that due

to change in bond strength, let us assume for the moment that the bonds in all these molecules will have the same elastic constant (k) as the normal homopolar bond between two carbon atoms. From a knowledge of the mass of the atom (m) we can then calculate the frequency of vibration (ν) from the formula

$$\nu = \frac{1}{2\pi} \sqrt{\frac{nk}{m}} \quad (1)$$

where n will be the average number of bonds which are effective for any displacement of the central atom. For the cases we are considering here, three- and four-valent atoms with the bonds uniformly distributed in space, n will probably have a value of about two. In this way the frequency of vibration of the metal atom has been calculated for eight of the compounds. Since it is customary in specific heat calculations to use the characteristic temperature θ which is equal to $h\nu/k$ (h , Planck's constant; k , Boltzmann's constant), the values of θ rather than of ν have been given in Table V.

From these the heat capacity due to the vibrations of the central atom can easily be calculated with the help of Einstein's formula for the heat capacity of an harmonic oscillator.⁴ Such values for three different temperatures are also given in Table V.

It may readily be seen that the increase in heat capacity due to this effect is not nearly large enough in most instances to account for the observed increase in heat capacity. Of course there may be other types of motion in the molecule for which increasing weight would change the heat capacity, but we might expect such a change to be more in the nature of a second order effect.

The change in heat capacity from carbon to silicon is perhaps the most striking in the whole group. This suggests the second effect which was mentioned above, namely, that due to the increase in the size of the central atom. It seems reasonable to suppose that in tetraphenylmethane the four phenyl groups are drawn in so close to the central carbon atom that their motions toward and away from each other are restricted to a considerable extent by their mutual fields of force. We would expect, then, as we pass to a larger central atom that this crowding would be eliminated, and that an increase in heat capacity would result, say, in passing from carbon to silicon, an increase which would become less marked in higher members of the series. This is certainly true as we pass from silicon to tin. Unfortunately data are not available for the densities of these compounds.

On the other hand, if we compare the tetravalent with the trivalent series we are immediately struck by the fact that the residue of heat capacity due to the central atom and to the molecule as a whole is almost identical for

⁴ See W. Nernst, "New Heat Theorem," E. P. Dutton, New York, for tables to simplify the calculation.

carbon and nitrogen. If the three bonds of nitrogen lie at approximately right angles to each other as Slater⁵ has deduced from wave mechanics, the crowding of phenyl groups might be just as great as in the case with carbon at the center. However, as we proceed along this series we find no striking increase in heat capacity like that experienced in going from carbon to silicon. This suggests that the increase in heat capacity is due to a weakening of the bonds. The fact that tetraphenyl tin has been used as a phenylating agent,⁶ while tetraphenylmethane has no such property, is also evidence in favor of this point of view.

One should also observe in this connection that among the hydrocarbons² the constancy of the increment in heat capacity due to a phenyl group when we pass from monophenyl to tetra- or pentaphenyl derivatives is an indication that crowding of the groups is not an important factor. The evidence therefore seems to be strongly in favor of the weakening of the bond forces as we go from low to high atomic weights. This is also in accord with the evidence from spectra in series such as the halogens.⁷ It is hoped that a more careful analysis, such as will be possible when further data from Raman spectra are available, will throw more light on this problem.

Summary

1. The heat capacities of mercury diphenyl, mercury di-*p*-tolyl, tetraphenylmethane, tetraphenylsilicane, tetraphenyl tin, triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, triphenylbismuthine, diphenyl oxide, diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone have been measured from 100 to 320°K. by the method of calibrated heat conduction.

2. Evidence is found of a weakening of the binding force between the phenyl groups and the central metal atom, as the weight of the latter increases.

BALTIMORE, MARYLAND

⁵ J. C. Slater, *Phys. Rev.*, **37**, 481 (1931).

⁶ Bost and Borgstrom, *THIS JOURNAL*, **51**, 1922 (1929).

⁷ J. R. Bates and D. H. Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928).