Physico-Chemical Studies on Molecular Compounds. III. Vapor Pressures of Diphenyl, 4, 4'-Dinitrodiphenyl, and Molecular Compound between Them

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Introduction

In a previous paper,[1] we have reported the vapor pressures of quinhydrone and of the molecular compound between hexamethylbenzene and picryl chloride. These molecular compounds (M. C.'s for brevity) are constructed with (1:1) molar ratio of the component molecules, and the benzene nuclei of them are arranged in nearly parallel positions alternately. Now, there are recently known some M. C.'s which are considerably different from those in the molecular arrangement as well as in their composition. According to James, Saunder, and others,[2] 4,4'-dinitrodiphenyl (D. N. D. for brevity) forms a number of M. C.'s with diphenyl and its derivatives. Their general type of crystal structure stands in contrast in such points as that the component molecules are packed in nearly perpendicular positions to each other and that the molar ratios differ from M. C. to M. C., giving no (1:1) molar ratios. In these respects, it will be of some interest to study the present materials in comparison with the substances already reported and also in relation to the urea-adducts[3] having some resemblance in their molecular arrangements, as well as to the molecular sieve actions of some zeolite crystals.[4]

Experimental

Apparatus.—The vapor pressures as well as the variations of composition of the solid phase as the evaporation proceeds were measured by the effusion method. The details of the apparatus were already reported in a previous paper,[5] so that its description may be omitted here.

Samples.—*Diphenyl*: The product "Zur Analyse" of Dr. Theodor Schuchart was recrystallized from glacial acetic acid solution. m. p. 69.5°~69.8°C.

D. N. D.: The material was prepared through nitration of diphenyl with fuming nitric acid, and then the product was recrystallized once from ethyl alcohol and further twice from acetone, finally being subjected to fractional sublimation under high vacuum (10^{-5} mm. Hg.) at about 120°C. m. p. 237.0°~237.5°C.

M. C. (1:3): Two acetone solutions containing diphenyl (somewhat in excess of the calculated 1:3 ratio) and D. N. D. were mixed at a little below the boiling point and then M. C. was precipitated by slow cooling of the mixture at a rate of about 10°C./hour. m. p. 194°~225°C.* The reason for such a wide range of melting process will be explained in a later section.

Results

The vapor pressures of diphenyl and D. N. D. are given in Tables 1 and 2 and illustrated in Fig. 1. The vapor pressure equations derived from them are also given in the bottoms of each table. The relation of the vapor pressures of (1:3) M. C. (vapor pressures

Table 1
Vapor Pressure Values of Diphenyl

t°C.	$P_{mm.Hg.} \times 10^3$
14.3	2.33
14.8	2.38
16.8	3.16
19.7	4.19
22.0	5.44
23.8	6.44
25.6	7.78
27.6	9.23
28.0	9.44
29.9	11.9
31.3	13.8
34.1	17.4

$$\log P = 11.003 - 3918.2/T$$
$$T = 273.14 + t$$

(1) I. Nitta, S. Seki, H. Chihara and K. Suzuki, *Sci. Papers Osaka Univ.*, No. 29 (1951).
(2) (a) W. S. Rapson, D. H. Saunder and E. T. Stewart, *J. Chem. Soc.*, **1946**, 1110; (b) D. H. Saunder, *Proc. Roy. Soc.*, **A190**, 508 (1947); (c) J. N. van Niekerk and D. H. Saunder *Acta Cryst.*, **1**, 44 (1948); (d) R. W. James and D. H. Saunder, *Proc. Roy. Soc.*, **A190**, 518 (1947).
(3) A. E. Smith, *Acta Cryst.*, **5**, 224 (1952).
(4) R. M. Barrer, *Quart. Rev.*, **3** 293 (1949).
(5) I. Nitta, S. Seki, M. Momotani and K. Sato, *J. Chem. Soc. Japan*, **71**, 378 (1950).

* Rapson et. al. 191°~221°C. see ref. (2a).

Table 2
Vapor Pressure Values of D. N. D.

t°C.	$P_{mm.Hg.} \times 10^3$
138.1	2.92
139.7	3.85
140.5	3.49
143.2	4.38
146.0	5.04
148.1	6.15
150.3	7.10
152.3	8.60
155.3	9.72

$\log P = 10.744 - 5458.2/T$

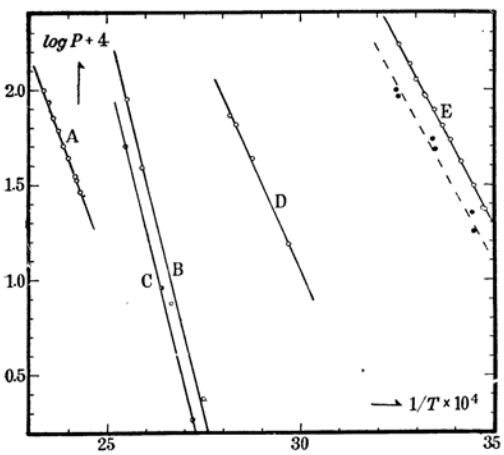

Fig. 1.—Vapor pressures of D. N. D. (A), (1:6) M. C. (B and C), (1:3) M. C. (D), and Diphenyl (E)
dotted line: Bright's values

calculated from the effusion velocity through an orifice of unit area) with the variation of effused amount are shown in Fig. 2. At relatively lower temperatures (e. g. curve (a) at 63.7°C. in the figure), the curves are composed of two regions: In the initial part, the vapor pressures are almost constant up to about 4.5% of the effused amounts, and then decrease remarkably. The position of the point B, at which the velocity begins to slow down, is more distinct at lower temperatures. But, as the temperature rises, the horizontal part (A-B) begins to incline downwards and the position of B becomes less distinct, moving to a region of somewhat smaller amounts of effusion. It is confirmed by the experiments that the material evaporated in the region (A-C) consists entirely of diphenyl. It is by the introduction of its molecular weight into the effusion equation that the vapor pressures at various stages of effusion as shown in the Fig. 2 are obtained. Extrapolating the curve to the zero point of effusion, we obtained the

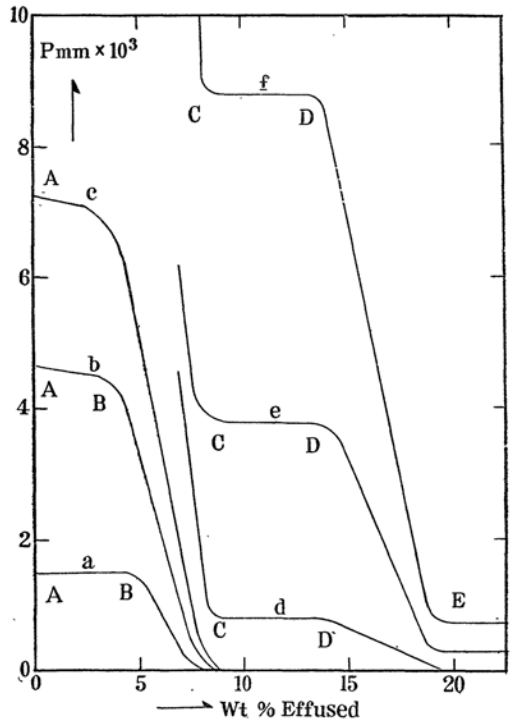

Fig. 2.—Vapor pressure change of M. C. with variation of effused amount
Experimental temperatures are as follows:
a: 63.7°C.; b: 74.5°C.; c: 79.9°C.;
d: 105.5°C.; e: 112.8°C.; f: 118.7°C.

Table 3
Vapor Pressure Values of (1:3) M. C.

t°C.	$P_{mm.Hg.} \times 10^3$
63.7	1.54
74.5	4.33
79.9	7.14
81.6	7.36

$\log P = 10.722 - 4555.9/T$

vapor pressure data of (1:3) M. C. at the initial stage of sublimation as given in Table 3 and Fig. 1. As the vapor pressure is increased by raising the temperature of the experiment, there appears another horizontal portion in the region exceeding about 8% of the effused amount. This composition is corresponding to nearly (1:6) molar ratio and the constancy of vapor pressure implies the occurence of another new sort of M. C. By the microscopic observation of the sample at this stage of effusion (8%), it is found that the original (1:3) M. C. is completely converted into another sort of woolly small crystalline aggregate, which shows a distinct melting point (m. p. 210°C.).

As is evident from Fig. 2, this horizontal

portion (C-D) is not inclined as the temperature rises and the position of point D remains always at the constant value of abscissa (13±0.5%) within the experimental error. The large portion of the material effused in the region of (C∼D) is found to be diphenyl. Since the determinations of the composition of effused substances by chemical analysis is difficult on account of their small amount, we have estimated the composition of the solid phase and molecular weight of effused substances approximately in the following manner. Assuming that the partial vapor pressures of D. N. D. are equal to those of pure D. N. D. at the same temperatures, then the value of abscissa at which the diphenyl molecules contained in the solid phase is exhausted may be calculated to be 18.6% from the observed rate of effusion and original composition of (1:3) M. C, In fact, the point where the vapor pressures reach those of pure D. N. D. is found to be 18.7±0.3%, proving the adequacy of the above assumption.

On this basis, the vapor pressures of (1:6) M. C. are calculated as given in Table 4 and Figs. 1 and 2. It was found also that the vapor pressures of this M. C. are influenced by the history of their preparation. That is, the product prepared from the decomposition of fresh (1:3) M. C. shows higher vapor pressures (line B in Fig. 1 and (a) in Table 4) than those from the (1:3) M. C. stored for about a month in a desiccator (line C in Fig. 1 and (b) in Table 4). The values of thermodynamic functions derived from the vapor pressure data of all the specimens are given in Table 5.

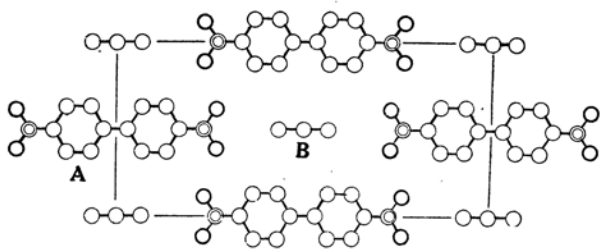

Fig. 3.—Idealized structure of a series of (1:3) M. C.
A: D. N. D. Molecules.
B: Diphenyl molecules or its derivatives.

Table 4
Vapor Pressure Values of (1:6) M. C.

(a)		(b)	
t°C.	$P_{mm.Hg.}\times10^3$	t°C.	$P_{mm.Hg.}\times10^3$
90.5	0.238	94.5	0.184
101.8	0.760	105.5	0.910
112.8	3.89	119.5	1.84
118.7	8.90		
$\log P=18.361-8016.2/T$		$\log P=18.987-8349.6/T$	

Although the final product beyond the point D shows the same Debye photograph as well as the same melting point with those of pure D. N. D., the vapor pressures are of a little higher values (not more than 5%) than the D. N. D. prepared by the ordinary method.*

Discussion

The results of vapor pressures obtained in the present investigation may be discussed first in comparison with the data already reported by other investigators. Among the substances measured by us, only the vapor pressure of diphenyl was measured by Wolf[6] and Bright.[7] The former reported merely a value of the heat of sublimation (16.4±0.2 kcal./mol.), which is considerably smaller than ours (17.9±0.4 kcal./mol.), while the heat of sublimation obtained by Bright(17.4±0.7 kcal./mol.) is in good agreement with ours, their vapor pressure values being, however, somewhat lower than ours as shown in Fig. 1.

Table 5
Enthalpy, Entropy and Standard Free Energy Changes of Sublimations*

Substances	ΔH kcal./mole	ΔS e. u./mole	$\Delta F^{298.1}$ kcal./mole
Diphenyl	17.94±0.41	37.14±1.36	6.89±0.81
(1:6) M. C. (a)	36.70±1.79	70.88±4.79	15.58±3.32
(1:6) M. C. (b)	38.23±0.70	73.75±1.86	16.24±1.25
(1:3) M. C.	20.86±0.41	35.90±1.44	10.15±0.84
D. N. D.	24.99±0.44	36.01±0.80	14.25±0.68

† The thermodynamic fuctions of M. C's are corresponding to those of their decomposition processes, in exact sense (see in the text).

* Similar facts were also found in the cases of α-quinol and picryl chloride produced by decomposition of the M. C.

(6) K. L. Wolf and H. Weghofer, *Z. Physik. Chem.* **B39**, 194 (1938).
(7) N. F. H. Bright, *J. Chem. Soc.*, **1951**, 624.

Now, we may proceed to the problems of M. C. Although the characteristic features of the crystal structure of the (1:3) M. C. were mentioned briefly in the last section, it may be desirable to explain them somewhat more in detail for the consideration of the evaporation processes. In this M. C., the D. N. D. molecules form layers in face-centered array, as shown in Fig. 3. The D. N. D. molecules A in the figure lying in this layer are so arranged that a gap is left between the nitro groups of adjacent D. N. D. molecules. By superposing such layers with a spacing of 3.5 A., these gaps will produce a set of tubular cavities, also in face-centered array, running through the whole structure. The molecules of diphenyl or its derivatives (B in Fig. 3) occupy these tubular cavities, as shown end-on in the figure. Thus the directions of the long axes of B molecules is exactly or nearly perpendicular to the layers containing D. N. D. molecules. The ratio of the number of B molecules to that of D. N. D. molecules varies from compound to compound, and depends on the length of B molecules rather than on their chemical nature, and, indeed, it has been found possible to predict the molar ratio in M. C. from a knowledge of such molecular length, indicating no localized bonding between A and B molecules. The non-integral ratio (1:3.33) of the M. C. with 4-chlorodiphenyl is the most remarkable example.[2a] [2d]

Turning to the evaporation process of (1:3) M. C., we can find a situation similar to that of the two M. C.'s reported in the previous paper,[1] i. e. the preferred evaporation of the more volatile component occurs, and the vapor pressures, the compositions of gaseous as well as of crystalline phase change with the progression of evaporation. When examined in more detail, however, the behavior of the M. C.'s of the present series is different in several points. As shown in Fig. 2 the vapor pressure-composition curve has, instead of one in the cases of previously reported substances, two horizontal regions followed by more gently sloped region than the M. C.'s previously reported.

From the standpoint of phase rule considerations, the horizontal parts, the constant pressure regions, which are independent on the compositions (A-B and C-D), mean the coexistence of one gas and two solid phases, whereas the other sloping regions (B-C and D. E) mean the presence of one gas and one solid phase.

In the cases of M. C.'s reported in a previous paper[1] the evaporation of the more volatile component necessitates the collapse of the original mother crystals on account of the features of the molecular arrangements in which each of the component molecules are piled up alternately. Accordingly, when the molecules of a more volatile component evaporate, the less volatile component molecules must be separated from the original crystals and recrystallized at a considerably rapid rate. Indeed, we obtained a wider range of horizontal parts of vapor pressures in these M. C.'s, implying that adequate conditions for the coexistence of the two solid phases are realized easily.

On the other hand, in the present M. C. the selective evaporation of the more volatile component would not necessitate the collapse of the mother crystals on account of the above mentioned structural characteristics. Indeed, the first horizontal parts (A-B) do not cover so wide a region as that of the M. C. previously reported and tend to slope at higher temperatures (e. g. the curve at 79.9°C.). This sloping tendency means the formation of a solid-solution-like structure resulting from the violent thermal motions of B component molecules along the tubular cavities.

Similar curves have been found recently in the hydrogen-titanium system by A. D. Mc. Quillan.[8] In this system, the lattice structure of titanium changes, appearing in the three types of interstitial compounds of α, β and γ, as the amount of hydrogen in the solid phase increases. In the midway regions between the definite composition of these interstitial compounds, they also show a solid-solution-like behavior. As is well known, such a phenomenon is frequently observed also in the hydration process of some sorts of gels and other hydrates[9] in which so-called "vagabond waters" are contained.

The wide range of melting phenomena observed in the present (1:3) M. C. described in the second section may be attributed to the formation of a solid solution owing to the partial evaporation of diphenyl. The comparison of the ΔH value of the (1:3) M. C. in Table 4 with that of the component crystals indicates also that the interaction of each component is not greatly strengthened by the formation of M. C.

When the amounts of effusion exceed about 8% of the original weight which corresponds to the molar ratio of about (1:6), the vapor pressure again retains a constant value, implying the coexistence of the two new solid phases. The existence of this (1:6) M. C. has

(8) A. D. Mc. Quillan, *Proc. Roy. Soc.*, **A204**, 309 (1951).
(9) W. Eitel, "Physikalische Chemie der Silikate", 1941, S. 517.

not been known yet for D. N. D.-diphenyl system. Such a large deviation of molar ratio from (1:1) may be very scarce for crystalline M. C. of aromatic nitrocompound-aromatic hydrocarbon (or aromatic amine, phenol) systems.* The distinct melting point (see section 2), the invariance of the flatness of vapor pressure in the region (C-D) as well as the constancy of the position of point D at various temperatures, and the values of thermodynamic functions given in Table 3 may be looked upon as the evidences of the considerably-stable structure of this (1:6) M. C. Although its crystal structure is not yet known, the mobility of the diphenyl molecule in this (C-D) region may be supposed to be restrained more strongly than the (1:3) M. C.

It is worth while to note, however, that the free energy of (1:6) M. C. prepared from two samples of the (1:3) M. C.'s which had been preserved for different periods of time, differs somewhat in each case. For the elucidation of this ageing effect, however, a further detailed investigation will be necessary.

In conclusion the authors wish to express their sincere thanks to Professor Nitta for his gracious encouragement and suggestions during this work. The expense of this investigation was defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Expenditure Grant from the Ministry of Education to which the authors' thanks are due.

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* It is known that the urea-adducts (see ref (3)), M. C. between desoxycholic acid and aliphatic long chain compounds (Y. Go and O. Kratky, *Z. Physik. Chem.*, **B26**, 439 (1934)), gas hydrate (W. F. Claussen, *J. Chem. Phys.*, **19**, 259 (1951); H. V. Stackelberg and H. R. Muller, *Naturwiss.*, **38**, 456 (1951) **39**, 20 (1952); L. Pauling and R. E. Marsh, *Proc. Nat. Acad. Art and Sci.*, Feb (1952)) and other so-called "clathrate compounds" (D. E. Powell, H. M. Powell, *J. Chem. Soc.*, **1947**, 208; **1948** 571, 815) show such anomalous molar ratio.