tensity of absorption is increased by a factor between 1.5 and 4. The vibrational structure is virtually unaltered. The effects of the $-PO_3H^-$ and the $-PO_3^=$ groups are even less than that of the phosphono group. The spectrum of benzenephosphonous acid is almost the same as that of benzenephosphonic acid. Diphenylphosphinic acid has a molar extinction twice that of benzenephosphonous acid; otherwise the secondary bands of the two compounds are practically identical. The absorption spectra of unsymmetrical diarylphosphinic acids ($Ar^IAr^{II}PO_2H$) can be calculated (to within 20%) by averaging the molar extinction coefficients of the corresponding symmetrical compounds ($Ar_2^IPO_2H$ and $Ar_2^{II}PO_2H$). This fact is illustrated in Fig. 3. The spectrum of triphenylphosphine oxide resembles the spectra of the other compounds in which "pentavalent" phosphorus is attached to a benzene ring.

For comparison with the compounds discussed above, the spectrum of triphenylphosphine was determined. This compound of trivalent phosphorus has a spectrum entirely different from that of the parent hydrocarbon. The vibrational structure typical of benzene is entirely lacking, and the extinction coefficients are much larger (*cf.* Fig. 4).

Discussion

According to Sklar,[6] a benzene derivative with considerable resonance between radical and ring has an ultraviolet absorption spectrum which differs markedly from that of the parent hydrocarbon. A purely inductive substituent on the other hand produces little intensification of the absorption. The relatively small effect of the phosphono and phosphinico groups suggests that no resonance exists between these groups and the aromatic nucleus. Therefore, it is probable that the phosphorus atoms of these substituents have no π-orbitals which can interact with the π-electrons of the benzene ring. This conclusion is consistent with the view that the P–O bond of the phosphoryl group[7] has no appreciable double bond character. The strong hyperchromic effect found in the spectrum of triphenylphosphine is doubtless due to extensive resonance between the phosphorus atom in this compound and the benzene nucleus. The fact that no such resonance is indicated by the spectrum of benzenephosphonous acid is further evidence for the so-called "keto" structure usually assigned to this compound.[8]

Robertson and Matsen[9] have pointed out that the dissimilarity between the spectra of compounds of the types $(C_6H_5)_2X$ and C_6H_5X is a measure of the degree of resonance interaction of the phenyl radical and the central atom. The similarity between the spectra of benzenephosphonous acid and diphenylphosphinic acid confirms the conclusion that no resonance exists between the benzene ring and the phosphorus atom in these compounds. Therefore, two aryl groups attached to a "pentavalent" phosphorus atom do not form a common conjugated system. This fact is consistent with the simple relationship found between the spectra of unsymmetrical phosphinic acids and the corresponding symmetrical acids.

Acknowledgment.—The authors wish to acknowledge the interest and helpful advice of Dr. G. O. Doak.

---

[6] A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939); *Rev. Mod. Phys.*, **14**, 232 (1942).

[7] The phosphoryl group is defined as the group $\equiv P—O$ in which the oxygen atom is bonded only to phosphorus.

[8] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 144; L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[9] W. W. Robertson and F. A. Matsen, THIS JOURNAL, **72**, 5250 (1950).

CHAPEL HILL, N. C. RECEIVED SEPTEMBER 12, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Melting of Binary Eutectics[1]

BY C. H. SORUM AND E. A. DURAND

Non-contact equilibrium fusion at the eutectic temperature has been observed for forty-five binary systems. A tentative picture of the fusion process is presented. This picture envisages a simple solid–vapor or solid–liquid transformation as the first step in the process and does not require the existence of solid solutions or solid–solid diffusion.

The changes that take place when a melt of two substances that form a simple binary eutectic is cooled, slowly, to complete solidification are pretty well understood.[2] Just exactly what happens when the solidified eutectic is melted is not quite so clear.

That the eutectic crystallizes in the form of a mixture of crystals of the pure components has been demonstrated by numerous investigations. That these are crystals of the pure components and not solid solutions has been proven by exact analysis and examination of the individual crystals.

It is a well known fact that when masses of two pure components which form a eutectic are brought in contact at the eutectic temperature invariant melting will take place.[2] That such melting does take place is further proof that the eutectic is in fact a mixture of pure crystals.

Experiments carried out in this Laboratory show that the pure crystals of the components of a binary eutectic will melt, invariantly, at the eutectic temperature even though these crystals are not in contact with each other. Proof is offered in Fig. 1 which illustrates the non-contact fusion of crystals of azobenzene and acenaphthene. The liquid droplets which form are of eutectic composition and the equilibrium temperature is the eutectic temperature. At

---

[1] Presented at the 117th A.C.S. Meeting, Detroit, Mich. This study was supported by a grant from the Wisconsin Alumni Research Foundation.

[2] H. W. K. Roozeboom, "Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," Vol. II, Part I, Braunschweig, 1904.

TABLE I

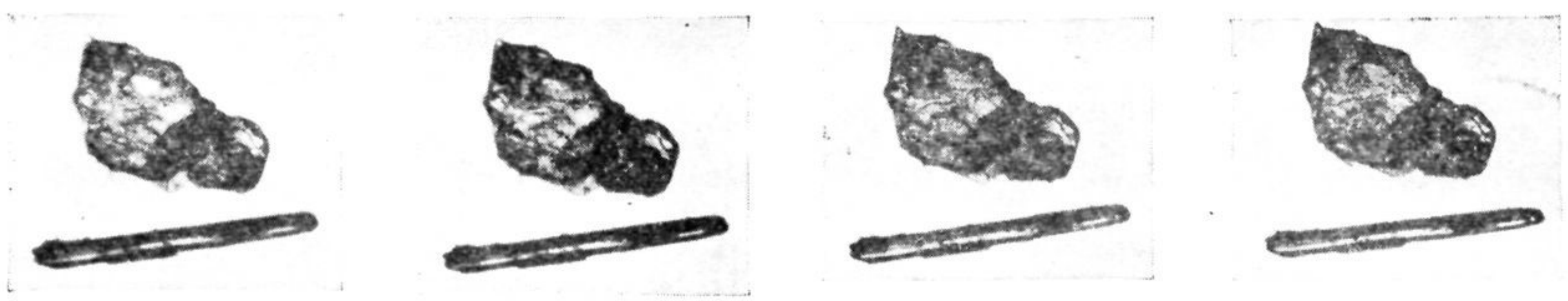
BINARY EUTECTICS SHOWING NON-CONTACT FUSION

No.	Component A	M.p., °C.	Component B	M.p., °C.	Eutectic temp., °C.	Fusion temp., °C.
1	Acetamide	79.0	Urethan	48.3	24.5	25.2
2	Acetamide	79.0	Benzoic acid	121.5	37.2	38.0
3	Acetamide	79.0	*o*-Nitrophenol	44.8	40.9	41.4
4	Azobenzene	67.0	*o*-Nitrophenol	44.8	29.0	30.0
5	Azobenzene	67.0	Acenaphthene	90.0	48.6	49.6
6	Azobenzene	67.0	α-Naphthol	95.5	44.9	46.0
7	Azobenzene	67.0	*p*-Nitrophenol	113.5	50.2	53.0
8	Azobenzene	67.0	β-Naphthol	121.0	51.6	55.1
9	Azobenzene	67.0	Benzil	92.7	52.3	54.0
10	Acenaphthene	90.0	*o*-Nitrophenol	44.5	32.9	34.1
11	Acenaphthene	90.0	Fluorene	112.5	61.0	64.0
12	Acenaphthene	90.0	Benzil	98.5	67.0	69.0
13	Acenaphthene	90.0	*p*-Nitrophenol	113.5	76.0	81.0
14	Acetanilide	113.0	*m*-Dinitrobenzene	90.2	68.0	71.0
15	Acetanilide	113.0	Urethan	48.3	39.0	39.6
16	α-Naphthol	92.0	Benzamide	124.8	39.0	39.6
17	α-Naphthol	95.5	Naphthalene	80.0	59.0	61.0
18	α-Naphthol	95.5	Succinimide	123.0	54.0	58.0
19	α-Naphthol	95.5	Cinnamic acid	133.0	65.0	69.0
20	Benzamide	124.8	β-Naphthol	122.0	56.9	60.0
21	Benzil	94.0	Benzoic acid	121.4	78.0	80.0
22	Benzoic acid	121.4	Naphthalene	80.1	69.0	72.0
23	Benzoic acid	121.4	Cinnamic acid	136.8	81.0	84.0
24	β-Naphthol	121.0	Cinnamic acid	133.0	82.0	85.0
25	Cinnamic acid	133.0	*p*-Nitrophenol	114.0	78.0	80.0
26	Cinnamic acid	133.0	Resorcinol	115.0	85.0	86.0
27	Coumarin	67.0	Naphthalene	80.1	42.1	44.0
28	Diphenyl	69.0	Naphthalene	80.1	39.6	40.6
29	Fluorene	112.5	2,4-Dinitrotoluene	69.5	41.0	43.1
30	Fluorene	112.5	*m*-Dinitrobenzene	89.0	49.1	51.2
31	Naphthalene	80.1	Fluorene	112.5	54.0	56.0
32	Naphthalene	80.1	Phthalic anhydride	130.8	60.0	62.0
33	Naphthalene	80.1	Thymol	49.2	32.1	34.0
34	Naphthalene	80.1	*p*-Dichlorobenzene	53.0	32.0	33.1
35	Naphthalene	80.1	*p*-Nitrotoluene	52.0	30.5	32.0
36	Naphthalene	80.1	*o*-Nitrophenol	45.0	30.2	30.8
37	Naphthalene	80.1	*p*-Nitrophenol	113.0	71.0	73.0
38	Resorcinol	115.0	Succinic acid	183.0	96.0	100.0
39	Urethan	48.3	*p*-Nitrotoluene	51.3	32.2	33.2
40	Urethan	48.3	*m*-Dinitrobenzene	90.0	39.0	39.6
41	*m*-Dinitrobenzene	89.9	2,4-Dinitrotoluene	69.5	40.6	43.2
42	*m*-Dinitrobenzene	89.9	*p*-Nitrotoluene	51.4	31.0	31.4
43	*o*-Nitrophenol	45.0	*p*-Dichlorobenzene	53.0	23.1	24.2
44	*o*-Nitrophenol	45.0	*p*-Nitrophenol	114.0	34.5	35.3
45	*p*-Nitrotoluene	51.4	2,4-Dinitrotoluene	70.1	30.3	32.1

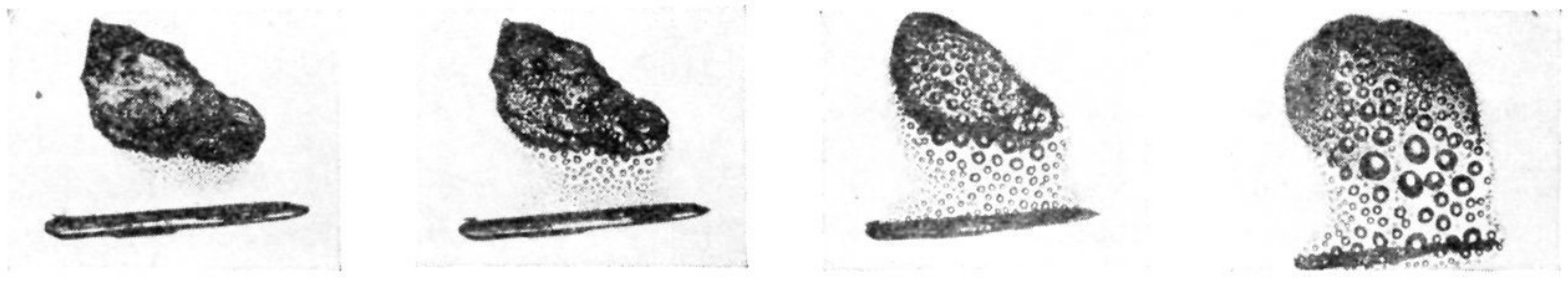
temperatures as little as 0.5° below the eutectic temperature no fusion takes place. Non-contact equilibrium fusion at the eutectic temperature has been observed for the 45 systems given in Table I.

The non-contact fusion studies were carried out with macro as well as semimicro quantities. In the former case the solids were placed in a small wide mouthed weighing bottle or covered crystallizing dish. The cover was sealed on, the bottle immersed in a water-bath at the eutectic temperature and the progress of the fusion observed through the bath windows. Semimicro quantities of crystals were placed in a small hermetically sealed cell whose top and bottom were round microscope cover glasses. The cell was maintained at, or slightly above, the eutectic temperature either by circulation of water through a jacket surrounding the cell or by means of an electrically heated hot stage. The progress of the fusion was observed through a microscope using crossed nicols in the light source. The "fusion temperatures" recorded in Table I are the temperatures of the hot stage or circulating water. The microscope method, although providing less accurate temperature control, gave a more vivid picture of the changes that took place. For a given system the greater the volume of the weighing bottle or cell the longer the time required for the appearance of a liquid phase. In the macro studies the liquid was first observed on the solid crystals. In the micro studies the droplets first appeared on the top cover glass because this glass, being exposed to the air, was undoubtedly cooler than the rest of the cell.

The observed non-contact melting of the pure components at the equilibrium eutectic temperature proves beyond any question that the existence of a solid solution is not necessary to account for the melting of a eutectic. Also, it rules out the need for assuming that molecules of one solid component diffuse into the other component as the first stage in the formation of the first drop of liquid of eutectic composition. Beyond that we can only say that eutectic melting appears to be a process in which molecules of the two components escape from the surfaces of the respective solids because these solids have appreciable vapor pressures. If the solids are surrounded by a gas the cycle is solid to mixed vapor to liquid solution. If there is no gas



1, after 1 hour at 47.6°. 2, after 3 min. at 49.6°. 3, after 18 min. at 49.6°. 4, after 30 min. at 50.6°.



5, after 2 hours at 50.6°. 6, after 4 hours at 50.6°. 7, after 8 hours at 50.6°. 8, after 12 hours at 50.6°.

Fig. 1.—Non-contact eutectic fusion of azobenzene (upper, irregular fragment; m.p. 67°) and acenaphthene (lower, elongated rod-like crystal; m.p. 90°) at 50.6°. Eutectic temperature 48.6°. 1, no evidence of fusion after 1 hour at 47.6°; 2 and 3, faint sign of droplets after 18 min. at 49.6°; 4, easily detectable droplets after 30 min. at 50.6°; 5, 6, 7 and 8, progressive accumulation of droplets and melting of solid components at 50.6°.

space the cycle is solid to liquid solution. There is, of course, no thermodynamic difficulty about the formation of a liquid solution from the two pure solids, not in physical contact, at or above the eutectic temperature. The solids are in thermodynamic contact through the vapor phase and the process considered, at constant temperature and virtually constant pressure, is accompanied by a decrease in free energy. The composition of the resulting vapor mixture and, hence, the composition of the liquid, would be expected to be determined by the vapor pressures of the two solids. The composition of the liquid is found to be that of the eutectic. How the composition of the gas phase is related to that of the liquid cannot be stated. Perhaps data on sublimation pressures which are now in the process of being gathered will throw more light on the picture. Since all eutectic systems are characterized by the fact that the components differ in crystal structure it may well be that all solid eutectics contain inter-crystalline spaces. If this is the case the cycle of eutectic melting may always be solid to vapor to solution.

MADISON, WISCONSIN RECEIVED MAY 25, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Quenching of the Fluorescence of Solutions of Porphyrins and of Chlorophyll[1]

BY ROBERT LIVINGSTON, LOU THOMPSON AND M. V. RAMARAO

The fluorescence of solutions of mesoporphyrin in benzene is quenched by the following substances: oxygen, 0.0028; chloranil, 0.0034; quinone, 0.0058; trinitrotoluene, 0.0062; *m*-dinitrobenzene, 0.011. The number following each compound is $[Q]_{1/2}$, the molarity of the quencher required to reduce the intensity of the fluorescence to one half of its unquenched value. Nine other compounds which were tested proved to be non-quenchers. The quenching efficiency for mesoporphyrin of each of these 14 compounds parallels in general their quenching efficiency for chlorophyll

The quenching of the fluorescence of chlorophyll-a solutions by each of a variety of added substances was measured recently,[2] as part of a program to study the primary act in photochemical processes involving chlorophyll. Most fluorescent solutions which have been studied, are quenched chiefly by reducing agents.[3] All of the compounds which effectively quench the fluorescence of chlorophyll solutions are oxidizing agents. It is of interest to know whether this latter group of quenchers is peculiar to chlorophyll or if it is characteristic of a group of molecules similar in some respects to chlorophyll. Accordingly, the quenching of solutions of mesoporphyrin and of protoporphyrin has been studied.

Experimental Methods and Materials

Except for the light filters, the apparatus and routine procedures were similar to those described by Livingston and Ke.[2] The λ 5460 Å. line was isolated from the radiation of a GE AH4 mercury arc by means of 2 cm. of 10% copper sulfate, a 4 mm. Corning 3486 and an 8 mm. Corning 5120 filter. The complementary filter, situated in front of the photocell, was a Wratten 88 which transmits light of wave lengths longer than 6000 Å.

The porphyrins used were samples of mesoporphyrin dimethyl ester and of protoporphyrin dimethyl ester,[4] whose final purification was effected chromatographically on activated alumina. The solvent used in these experiments was benzene, which was prepared from "thiophene-free" mate-

---

(1) This work was made possible by the support of the Office of Naval Research (NR 059, 028, Contract N6ori-212, T.O. I) and by a grant from the Graduate School of the University of Minnesota to whom the authors wish to express their indebtedness.

(2) R. Livingston and Chun-Lin Ke, THIS JOURNAL, **72**, 909 (1950).

(3) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, pp. 328–335.

(4) We wish to express our thanks to Dr. S. Schwartz of the Medical School of the University of Minnesota who kindly put those samples at our disposal.