Experimental

Thiophene-2-glyoxal *n*-Heptylhemimercaptal.—Fourteen grams (0.1 mole) of thiophene-2-glyoxal was mixed with 13.2 g. (0.1 mole) of *n*-heptyl mercaptan. A considerable amount of heat was generated, and on allowing the mixture to cool to room temperature, the entire mass crystallized. The product was purified by recrystallization from heptane, giving colorless crystals melting at 76–77° d.

The other hemimercaptals were prepared in a similar manner.

MORRIS PLAINS, N. J. RECEIVED OCTOBER 11, 1951

[CONTRIBUTION FROM VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra of Arylphosphonic and Diarylphosphinic Acids

BY H. H. JAFFÉ AND LEON D. FREEDMAN

The ultraviolet absorption spectra of a number of arylphosphonic and diarylphosphinic acids, and of a few related compounds have been determined. These spectra indicate that no resonance exists between a "pentavalent" phosphorus atom and an aromatic nucleus attached to it and that the P–O bond in the phosphoryl group has no appreciable double bond character. Evidence is also presented which confirms the "keto" structure usually assigned to benzenephosphonous acid.

In connection with a study of certain organic phosphorus compounds in this Laboratory, it appeared desirable to investigate the effect of the phosphono ($-PO_3H_2$) and phosphinico ($>PO_2H$) groups on the ultraviolet absorption spectra of benzene and its derivatives. The present paper describes the results obtained with arylphosphonic acids, diarylphosphinic acids and a few related compounds.

TABLE I

Compound	Primary band λmax. mμ	Primary band εmax.	Secondary band λmax. mμ	Secondary band εmax.
C_6H_6			254.5	180
$C_6H_5PO_3H_2$			263.5	524
$C_6H_5PO_3H^-$			263.0	383
$C_6H_5PO_3^{=}$			258.0	239
$C_6H_5PO_2H_2$	216	7,100	264.5	616
$C_6H_5PO_2H^-$			263.5	477
$(C_6H_5)_2PO_2H$	224	13,100	265.0	1,200
$(C_6H_5)_2PO_2^-$	222	12,000	264.0	882
$(C_6H_5)_3PO$	224	21,300	265.5	2,420
$(C_6H_5)_3P$[a]			261[b]	11,000[b]
ClC_6H_5			264.0	206
o-$ClC_6H_4PO_3H_2$	217	12,300	270.5	798
m-$ClC_6H_4PO_3H_2$	215	8,130	271.0	649
p-$ClC_6H_4PO_3H_2$	224	14,400	264.0	292
(*o*-$ClC_6H_4)_2PO_2H$			273.5	1,738
(*m*-$ClC_6H_4)_2PO_2H$			273.0	1,390
(*p*-$ClC_6H_4)_2PO_2H$[c]	234	22,200	265.0	1,000
$NO_2C_6H_5$	260	7,100		
m-$NO_2C_6H_4PO_3H_2$	263	6,400		
p-$NO_2C_6H_4PO_3H_2$[d]	270	10,400		
p-$NO_2C_6H_4PO_3H^-$	272	10,800		
p-$NO_2C_6H_4PO_3^{=}$[e]	278	10,300		
(*m*-$NO_2C_6H_4)_2PO_2H$[f]	263	14,300		
(*p*-$NO_2C_6H_4)_2PO_2H$	274	21,100		
(*p*-$NO_2C_6H_4)_2PO_2^-$	272	21,400		
(*m*-$ClC_6H_4)C_6H_5PO_2H$			272.5	1,250
(*m*-$NO_2C_6H_4)C_6H_5PO_2H$[g]	263	7,570		
(*p*-$NO_2C_6H_4)C_6H_5PO_2H$	272	11,500		
(*p*-$NO_2C_6H_4)C_6H_5PO_2^-$	272	11,500		

[a] The spectrum of this compound has been previously determined by J. E. Purvis, *J. Chem. Soc.*, 105, 1372 (1914). [b] It is uncertain whether these values should be assigned to the primary or secondary band. [c] The purity of this compound was doubted at first when the spectrum was determined and the strong absorption band at 234 mμ was observed. Therefore, the compound was recrystallized two more times from dilute alcohol; no change in the spectrum was noted. [d] Secondary primary band; $\lambda_{max.}$ 213, $\epsilon_{max.}$ 5,950. [e] Second primary band: $\lambda_{max.}$ 216, $\epsilon_{max.}$ 5,580. [f] Second primary band: $\lambda_{max.}$ 218, $\epsilon_{max.}$ 26,100. [g] Second primary band: $\lambda_{max.}$ 220, $\epsilon_{max.}$ 19,600.

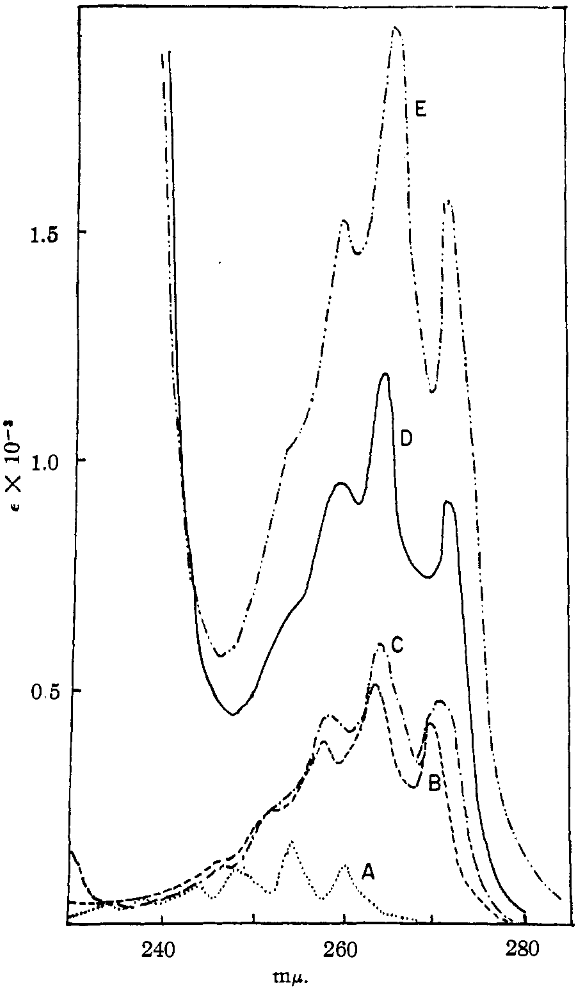

Fig. 1.—Absorption spectra: A, benzene; B, benzenephosphonic acid; C, benzenephosphonous acid; D, diphenylphosphinic acid; E, triphenylphosphine oxide.

Experimental

All compounds studied were prepared in this Laboratory. The synthesis of the arylphosphonic and the symmetrical

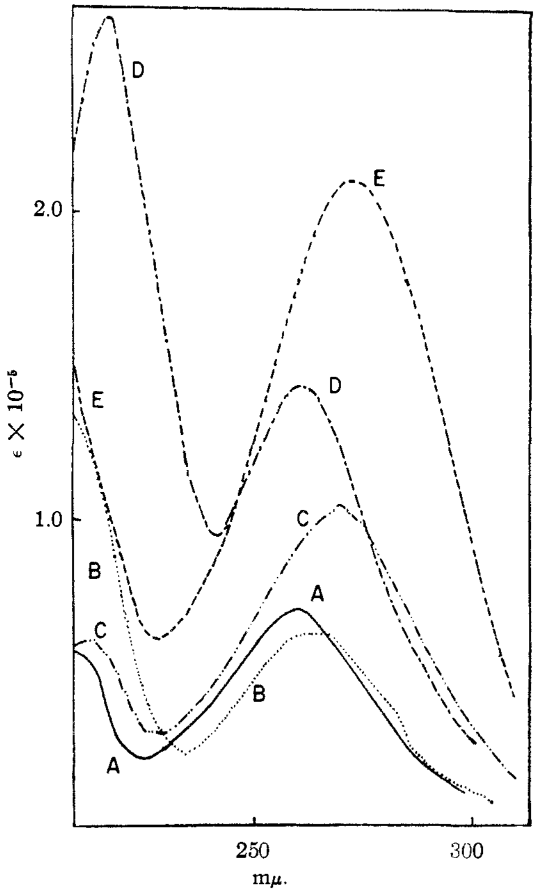

Fig. 2.—Absorption spectra: A, nitrobenzene; B, *m*-nitrobenzenephosphonic acid; C, *p*-nitrobenzenephosphonic acid; D, bis-(*m*-nitrophenyl)-phosphinic acid; E, bis-(*p*-nitrophenyl)-phosphinic acid.

diarylphosphinic acids has been described recently.[1] The preparation of the unsymmetrical phosphinic acids will be reported in a later paper. Triphenylphosphine,[2] triphenylphosphine oxide[3] and benzenephosphonous acid[4] were prepared by known methods.

Spectra of anions were determined in aqueous solution. Ethyl alcohol (95%) was used as the solvent for all other compounds. It was transparent above 210 mμ.

A Beckman model DU quartz spectrophotometer was used for the absorption measurements. Readings were taken at 2 mμ intervals, except in the neighborhood of the steep vibrational peaks, where readings were taken at 0.5-mμ intervals. All readings were in the optical density interval from 0.125 to 0.800 and the extinctions at the maxima were calculated from optical density values between 0.300 and 0.800.

Results

Table I lists the wave lengths of the "primary" and "secondary" absorption maxima[5] and the molar extinction coefficients at these maxima. The absorption spectra of several representative compounds are plotted in Figs. 1–4.

It is apparent from the recorded data that the phosphono group causes no profound change in the general characteristics of the spectrum of the parent compound. The secondary band shows a bathochromic shift of less than 10 mμ and the in-

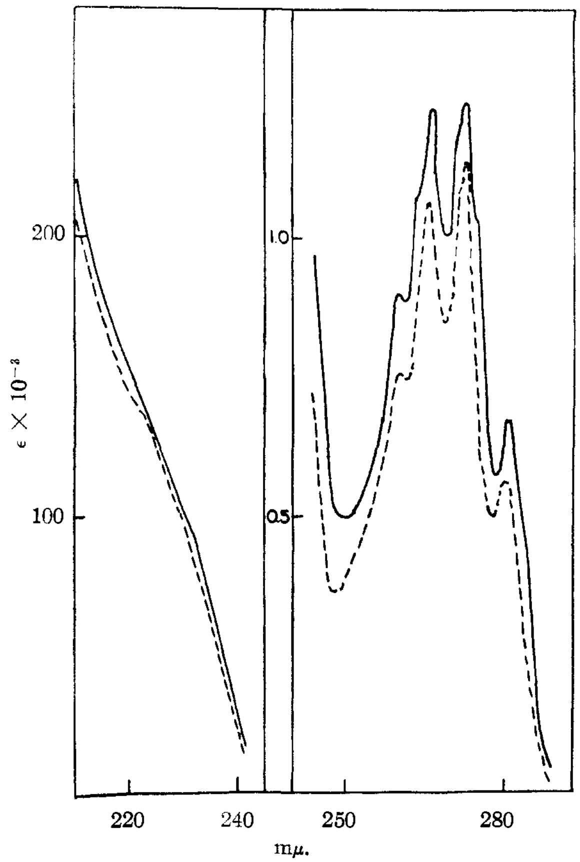

Fig. 3.—The absorption spectrum of (*m*-chlorophenyl)-phenylphosphinic acid: —, found; - - - -, calcd.

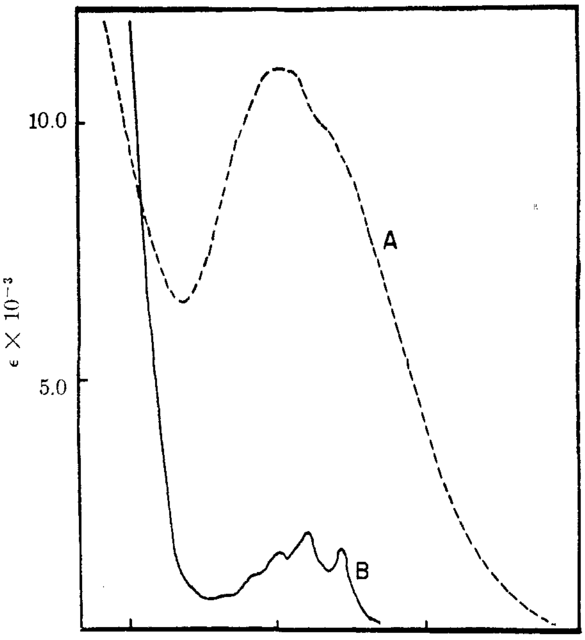

Fig. 4.—Absorption spectra: A, triphenylphosphine; B, triphenylphosphine oxide.

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(1) G. O. Doak and L. D. Freedman, This Journal, **73**, 5658 (1951).

(2) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 296.

(3) H. Gilman and G. E. Brown, This Journal, **67**, 824 (1945).

(4) G. M. Kosolapoff and J. S. Powell, *ibid.*, **72**, 4291 (1950).

(5) The terms "primary" and "secondary" bands are used in accordance with the definitions of L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

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.

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[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

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[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.