

oxazalone were obtained from these compounds isolated by fractional crystallizations as by-products from the preparation of the 2-phenyl derivatives. In each case, there is still about 5–15% of the 2-phenyl derivative present. The effect of variables such as time of heating and temperature on the rate of transacylation can now be readily investigated since

the reaction has been shown to occur with readily available compounds as well as with the more difficultly obtainable fluorobenzaldehyde azlactones.

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Experiments in the 1,2-Di-(γ -pyridyl)-ethane Series¹

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1,2-Di-(γ -pyridyl)-ethane and its methiodide are readily oxidized to the corresponding ethylene derivatives. The two bases form mixed crystals, as do their salts. The ethylene absorbs strongly at 295 $m\mu$, where stilbene has its absorption. A pronounced bathochromic shift occurs on methiodation; the bismethiodide of the ethylene absorbs at 315 $m\mu$, approximately where diphenylbutadiene absorbs. Both methiodides show a much stronger absorption at 225 $m\mu$ than tetraalkylammonium iodides; furthermore, the (solid) ethane methiodide is yellow and the ethylene methiodide is ruby-red, while the methobromides and methonitrates of both bases are colorless. A marked deformation of the iodide ion by the pyridinium ion is therefore indicated. Chloranil forms a brown-violet addition compound with 1,2-di-(γ -pyridyl)-ethane, which peptizes in water.

The immediate purpose of the present investigation was the elucidation of a number of puzzling observations made in the course of the preparation of 1,2-di-(γ -pyridyl)-ethane and -ethylene³ dimethiodides. When the ethane compound was quaternized and the product subjected to fractional crystallization, vividly colored fractions, ranging from yellow to ruby-red, were obtained; in particular, upon prolonged standing, crystallizates of intensely red color were observed. Investigation has shown that the red product was the dimethiodide of the ethylene and that the color variation was due to the presence of varying amounts of the unsaturated quaternary salt mixed with the dimethiodide of the saturated compound. This behavior was traced to two causes. First, 1,2-di-(γ -pyridyl)-ethane and -ethylene cannot be separated completely by crystallization, as described by Thayer and Corson³; the bases, as well as their methiodides, appear to form mixed crystals, in the same manner as dibenzyl and stilbene.⁴ Incidentally, this seems to prove that the ethylene is the *trans*-form as *cis*-isomers are known not to give mixed crystals with the corresponding saturated compounds. Second, the saturated dimethiodide, when its solution is exposed to air, is gradually dehydrogenated to the unsaturated quaternary salt. This oxidation is undoubtedly due to the particular nature of the 1,2-diarylethane compounds, which involves a large contribution from hyperconjugated forms.⁵ Thayer and Corson³ have already commented on the relative ease of the dehydrogenation of the ethane. It has now been

shown that the ethane reacts smoothly with N-bromosuccinimide, giving the hydrobromide of 1,2-di-(γ -pyridyl)-ethylene.⁶ Another significant observation was made: when the ethane was added to a solution of chloranil in xylene, a dark-brown, quinhydrone-like compound precipitated. This suggests that the ethane has the character of a hydroquinone, the quinone form obviously being the 1,2-di-(γ -pyridyl)-ethylene.^{7,8}

Spectral analysis provided an accurate method of characterizing the various compounds. Furthermore, it was found that the solubilities of the two dimethiodides in nitroparaffins are so different that they can be prepared in quite pure form by recrystallization of the ethane compound from nitromethane, in which the ethylene dimethiodide is only very slightly soluble, while the latter can be recrystallized from 1-nitropropane. The former gives well-shaped yellow prisms, the latter fine brown-red needles. Figure 1 shows the two spectra; it also includes an example of an "orange" salt which was obtained in the course of a lengthy (and unsuccessful) fractional crystallization of the ethane dimethiodide. The ethylene dimethiodide has a very sharp maximum at 315 $m\mu$ (ϵ 41,000), while the ethane salt has no absorption in this region, but a maximum at 255 $m\mu$ (ϵ 8,000). The visible spectrum of both methiodides shows no distinct bands but a gradually decreasing absorption as one proceeds from 360 to 500 $m\mu$ (ethane, ϵ 16.4 to 0.097; ethylene, ϵ 294 to 16.1; Fig. 2). It is surprising that the red ethylene bismethiodide is only yellow in aqueous solution.

The shift in the ultraviolet spectra of the ethane

(1) Paper No. 34 of Project NR 002-054 of the Office of Naval Research.

(2) Weizmann Institute of Science; Woodward lecturer, Yale University, March, 1952.

(3) H. I. Thayer and B. B. Corson, *THIS JOURNAL*, **70**, 2331 (1948).

(4) G. Biuni, quoted by G. Wittig, "Stereochemie," Akademische Verlagsgesellschaft, Leipzig, 1930, p. 318; P. Pascal and L. Normand, *Bull. soc. chim.*, [4] **13**, 154 (1913).

(5) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc, New York, N. Y., 1941, p. 116.

(6) For the reaction of *sym*-diarylethanes with N-bromosuccinimide, see R. A. Barnes, *THIS JOURNAL*, **70**, 145 (1948); E. Bergmann and J. Szmuszkowicz, *ibid.*, **73**, 5153 (1951).

(7) For the dehydrogenation of *sym*-diarylethanes by chloranil, see E. Buchta and W. Kallert, *Ann.*, **573**, 227 (1951).

(8) For the dehydrogenation of hydrogenated heterocyclic compounds by chloranil, see Ng. Ph. Buu-Hoi, Ng. Hoan and Ng. D. Xuong, *J. Chem. Soc.*, 279 (1952).

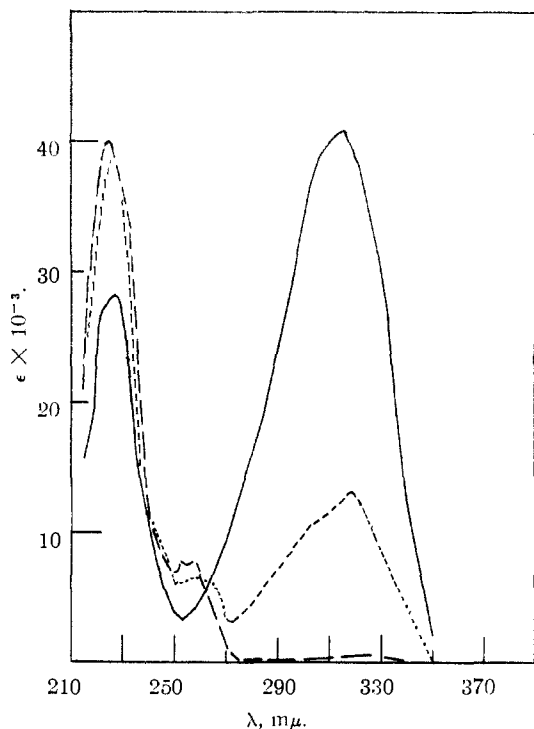


Fig. 1.—Absorption spectra: solid curve, 1,2-di-(γ -pyridyl)-ethylene methiodide; dashed curve, 1,2-di-(γ -pyridyl)-ethane methiodide; dotted curve, "orange" salt. (The molar extinction coefficient ϵ is defined by $\log I_0/I = \epsilon cl$, where c is concentration in moles per liter and l is cell thickness in cm. Our measurements were made at room temperature in quartz cells one cm. thick; concentrations usually were of the order of 10^{-4} molar.)

and ethylene compounds is unexpectedly large. This is illustrated by the following comparison with the pair stilbene-dibenzyl: dibenzyl,^{9,10} 259 $m\mu$, ϵ 360; 203 $m\mu$, 30,000; 198 $m\mu$, 105,000; stilbene,^{10,11} 295 $m\mu$, ϵ 27,000; 226 $m\mu$, 20,000; 220 $m\mu$, 25,000; ethane dimethiodide, 255 $m\mu$, ϵ 8,000; ethylene dimethiodide, 315 $m\mu$, ϵ 41,000. While the two saturated compounds absorb at the same wave length (for the longest absorption band), the dimethiodide has a much higher extinction coefficient than the hydrocarbon, undoubtedly due to the increase of the excitability of the absorbing system by the positive charge of the pyridinium nitrogens. In the unsaturated dimethiodide, the absorbing system has been extended considerably, and the position of the longest absorption band corresponds to diphenylbutadiene¹² rather than to stilbene.

It was shown that adsorption of the ethane from benzene solution on activated alumina and subsequent elution with chloroform affords a satisfactory fractionation, the first fraction being free of ethylene which appears in later fractions in increasing quantities. Likewise, the ethylene proved not to be completely free of the ethane; the same proce-

(9) It is interesting to recall that dibenzyl cannot easily be obtained free from stilbene: R. Lucas, *Compt. rend.*, **192**, 53 (1931).

(10) H. Ley and H. Dirking, *Ber.*, **67**, 1331 (1934).

(11) A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931).

(12) K. W. Hausser, R. Kuhn and G. Seitz, *ibid.*, **B29**, 391 (1935).

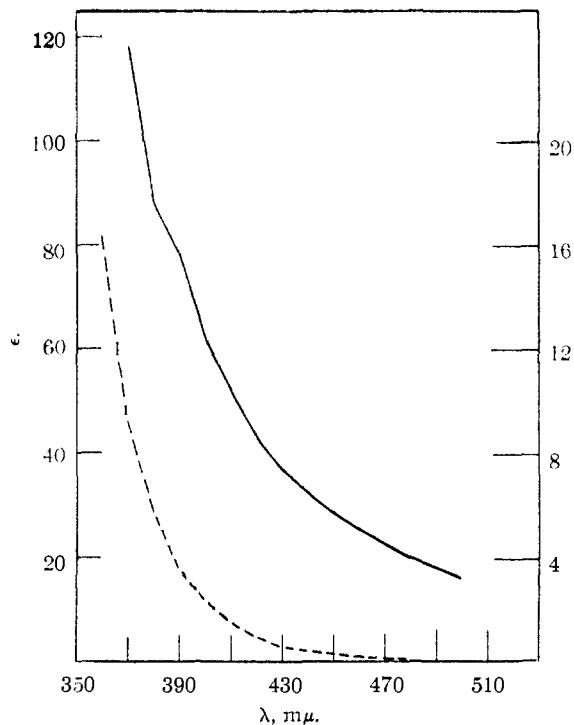


Fig. 2.—Absorption in the visible range; 1,2-di-(γ -pyridyl)-ethane methiodide, dotted curve, ordinates right; 1,2-di-(γ -pyridyl)-ethylene methiodide, solid curve, ordinates left.

dure yielded a first fraction containing a definite amount of ethane from which the later fractions were free. Both the ethane and ethylene absorb at the same wave lengths as dibenzyl and stilbene, respectively.

This investigation uncovered another peculiar effect related to the absorption of the iodide ion. As Fig. 1 shows, both the ethylene and ethane dimethiodides have a very pronounced band at 225 $m\mu$, the extinction coefficient being of the order of magnitude of 40,000. In our opinion, this is the absorption of the iodide ion which Fromherz and Menschick¹³ found in water at 227.3 $m\mu$ (ϵ 12,500) and in alcohol at 196 $m\mu$ (ϵ 12,500). The spectra of the methiodides of pyridine¹⁴ and of γ -picoline were also measured: pyridine, 260 $m\mu$, ϵ 4,240; 225 $m\mu$, 11,600; γ -picoline, 255 $m\mu$, ϵ 6,500; 225 $m\mu$, 29,300. The somewhat puzzling point is that tetraalkylammonium iodides absorb at the same wave length but with considerably lower intensity. Thus, for tetramethylammonium iodide, a molecular extinction coefficient of 13,300 and for several other iodides ϵ -values of 15,200, 19,900 and 20,900 have been reported by Knight, *et al.*¹⁵ Tetramethylammonium bromide, tetrabutylammonium bromide and nitrate do not exhibit any selective absorption in the near ultraviolet; the bromides from 230 $m\mu$ and the nitrate from 250 $m\mu$ onwards show a very intense end absorption, which for the

(13) H. Fromherz and W. Menschick, *ibid.*, **B7**, 439 (1930); *cf.* also G. Scheibe, *Ber.*, **59**, 1321 (1926).

(14) A. Hantzsch, *ibid.*, **44**, 783 (1911), observed for pyridine methiodide in alcohol a band at 233 $m\mu$, and in chloroform two bands at 278 and 328 $m\mu$.

(15) S. B. Knight, R. W. Bost, O. L. Shealy and J. P. Williams, *THIS JOURNAL*, **73**, 29 (1951).

nitrate is undoubtedly identical with that observed by Scheibe.¹¹ As also pyridine methochloride shows in this region an increase in extinction but no defined absorption,¹⁶ the increase in extinction coefficient cannot be due to a superposition of the iodide band and a pyridinium band. This can also be concluded from the fact that pyridinium salts (for instance, the sulfate) only show the same absorption at 256 $m\mu$ as pyridine, but with greater intensity.^{17,18} One has to conclude that the N-alkylpyridinium ion causes a greater deformation of the iodide ion than either alkali or other organic ammonium ions. This is also the reason for the intense colors of the solid salts, to which reference has been made above, and should be reflected in the ionic refraction of the iodide ion in these compounds. It should also be pointed out that the bismethonitrate and bismethobromides of the dipyrindylethane and -ethylene are colorless both in the solid state and in solution, but an orange-yellow color immediately appears on mixing aqueous solutions of the methonitrate or methobromide of the ethylene with potassium iodide solution.

Experimental

1,2-(Di- γ -pyridyl)-ethane and -ethylene were prepared according to the literature.³ Recrystallization of the ethane from a mixture (3:1) of cyclohexane and benzene give a material of m.p. 114.5–116.0° (lit. 110–111°).

Anal. Calcd. for $C_{12}H_{12}N_2$: N, 15.2. Found: N, 15.2, 15.1.

The ethylene was recrystallized three times from water; white needles, m.p. 155.5–156.5°.

1,2-Di-(γ -pyridyl)-ethane Bismethiodide.—An alcoholic solution in the ratio of 1 mole of the ethane and 6 moles of methyl iodide was kept at room temperature for 12 hours. Orange crystals separated. Upon prolonged standing, the mother liquor deposited a second crop of yellow to orange crystals together with a few ruby-red ones. The first crop was repeatedly recrystallized from a small quantity (10 cc. per g.) of nitromethane and was thus obtained in form of glistening prisms of yellow color, m.p. 322° (dec.).

Anal. Calcd. for $C_{14}H_{16}N_4I_2$: I, 54.22. Found: I, 54.15.

Similar observations were made in the iodothylation of the ethane derivative.

1,2-Di-(γ -pyridyl)-ethylene Bismethiodide.—To the solution of 0.41 g. of the ethylene in 15 cc. of 95% alcohol, 1.5 cc. of methyl iodide was added; the mixture, which turned yellow instantaneously, was kept at room temperature for 20 hours. After that time, it had become red, and orange-red crystals had begun to separate. The flask was cooled to ice-salt temperature and the solid filtered and washed with alcohol. Recrystallization from 1-nitropropane (100 cc. per g.) gave brown-red needles, m.p. 235° (dec.), yield 0.54 g. (54%).

Anal. Calcd. for $C_{14}H_{16}N_4I_2$: I, 54.46. Found: I, 54.16.

The same substance, which is only very slightly soluble even in boiling nitromethane, is also obtained by a recrystallization of the red products isolated from the mother liquors of the ethane bismethiodide. Furthermore, a sample of the red product gave on sublimation at 330° and 2 mm. an orange coated sublimate; the latter gave light tan crystals from water. Their melting point was 149–152° and the spectrum in 95% ethanol had a maximum at 295 $m\mu$ with ϵ 25,200, agreeing closely with the values found for the pure ethylene. These results clearly show that the bismethiodide of the ethane is oxidized by air to the ethylene derivative.

1,2-Di-(γ -pyridyl)-ethylene Monomethiodide.—From the mother liquors in the preparation of the bismethiodide of the

ethylene, orange-yellow crystals were obtained. They were identified as the monoaddition product.

Anal. Calcd. for $C_{13}H_{13}N_3I$: I, 39.15. Found: I, 39.56.

Bismethobromide from 1,2-Di-(γ -pyridyl)-ethane. (a).—A mixture of 10 g. of methyl bromide and 1.2 g. of the ethane in 25 cc. of 95% alcohol was kept at 15° for ten hours. Upon chilling with ice, the colorless bismethobromide crystallized. It decomposes at 330–335° and turns slowly yellowish upon standing.

Anal. Calcd. for $C_{14}H_{16}N_4Br_2$: Br, 42.7. Found: Br, 42.8.

(b).—A solution of 0.33 g. of an orange-yellow preparation of the bismethiodide in 20 cc. of distilled water was stirred with 4 g. of freshly prepared silver bromide for 8 hours. The filtered solution, which gave a negative test for iodide ion was concentrated to dryness *in vacuo*. The bismethobromide so obtained was colorless. Spectra: (a) 315–320 $m\mu$, ϵ 2,320, 255 $m\mu$, 7,940; (b) 315 $m\mu$, ϵ 6,940, 255 $m\mu$, 8,580.

The presence of varying amounts of the 1,2-di-(γ -pyridyl)-ethylene salt is very conspicuous.

Bismethonitrate from 1,2-Di-(γ -pyridyl)-ethane.—This was prepared from the above two bismethobromides by treating the aqueous solutions with the theoretical quantity of silver nitrate at 25°. The filtered solutions, upon concentration *in vacuo*, gave colorless crystalline residues. The absorption spectra were practically identical with those of the bromides: (a) 315–320 $m\mu$, ϵ 2,480; 255 $m\mu$, 8,120. (b) 315 $m\mu$, ϵ 6,230; 255 $m\mu$, 7,750.

1,2-Di-(γ -pyridyl)-ethylene bismethonitrate was prepared by metathesis with an exact equivalent of silver nitrate in aqueous solution from the bismethiodide. The mixture was heated to coagulate silver iodide, and filtered; the filtrate tested negative for both silver and iodide ion. Evaporation at 60° and 20 mm. gave a white residue which was recrystallized from 95% ethanol; silky needles, m.p. 280°, with decomposition.

Anal. Calcd. for $C_{14}H_{16}N_4O_6$: N, 16.67. Found: N, 15.70 (Dumas).

1,2-Di-(γ -pyridyl)-ethane methosulfate was prepared from 1.1 g. of the ethane in 15 ml. of 95% ethanol by the addition of 2.5 ml. of dimethyl sulfate. After 5 days, the solution was evaporated to dryness under reduced pressure. The white residue melted at 150°. A sample was dissolved in water and treated with an equivalent of barium iodide solution. The mixture turned yellow immediately. After filtering out the barium methyl sulfate, the solution was allowed to stand. Some yellow crystals formed after partial evaporation; those in contact with the air turned orange overnight.

Pyridine methiodide was prepared from 16.1 g. of methyl iodide and 8.9 g. of pyridine in 40 cc. of absolute ethanol. The yellow solution was heated for 10 min. at 45° and then kept at room temperature for 16 hours. When seeded, it solidified with evolution of heat. The product was recrystallized from alcohol; m.p. 123–125°, lit.¹⁹ 117°, yield 21.7 g.

γ -Picoline Methiodide.—When 45.0 g. of methyl iodide, 22.8 g. of γ -picoline and 46.0 g. of anhydrous alcohol were heated at 45°, an exothermic reaction set in. After it had subsided, the solution was brought to room temperature and seeded. The product was filtered after 10 hours and recrystallized from anhydrous alcohol; white needles, m.p.²⁰ 157–158°, yield 35 g.

Tetramethylammonium bromide was a commercial product which was recrystallized twice from 95% ethyl alcohol.

Tetra-*n*-butylammonium bromide was prepared according to Hager and Marvel²¹ and Sadek and Fuoss.²² Recrystallization from a mixture of benzene and petroleum ether (4.5:1) gives colorless crystals of m.p. 123–124°.

Anal. Calcd. for $C_{16}H_{36}NBr$: Br, 24.8. Found: Br, 24.8, 24.9 (potentiometric titration).

Tetra-*n*-butylammonium nitrate was prepared according to Cox, Kraus and Fuoss.²³

Reaction of N-Bromosuccinimide with 1,2-Di-(γ -pyridyl)-ethane.—A solution of 1.8 g. of the ethane compound in 50

(19) A. P. Prescott, *ibid.*, **18**, 91 (1896).

(20) P. Murrill, *ibid.*, **21**, 828 (1899), does not record the melting point.

(21) F. D. Hager and C. J. Marvel, *ibid.*, **48**, 2689 (1926).

(22) H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950).

(23) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **168**, 749 (1935); R. M. Fuoss, *THIS JOURNAL*, **55**, 21 (1933).

(16) P. Krumholz, *THIS JOURNAL*, **73**, 3487 (1951).

(17) E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 410 (1949).

(18) M. L. Swain, A. Eisner, C. S. Woodward and B. A. Brice, *THIS JOURNAL*, **71**, 1341 (1949).

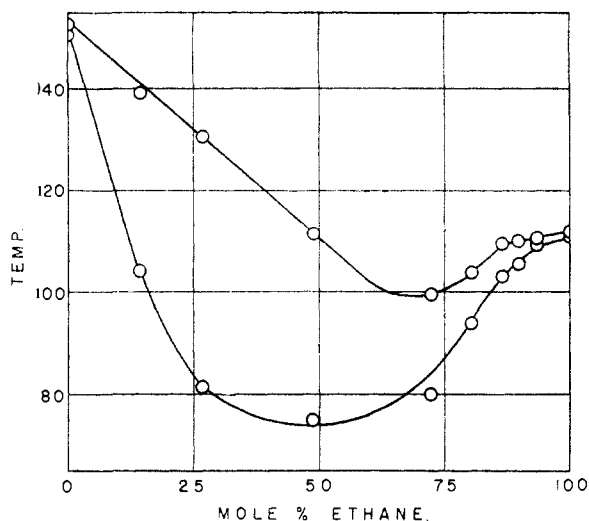


Fig. 3.—Phase diagram for 1,2-di-(γ -pyridyl)-ethane and ethylene.

cc. of carbon tetrachloride was refluxed for 2 hours with 1.8 g. of *N*-bromosuccinimide and 0.1 g. of benzoyl peroxide. The filtered hot solution, from which crystals separated spontaneously upon cooling, was brought to dryness. The residue, recrystallized from *s*-butanol, formed silky needles of m.p. 265° (dec.). It was the monohydrobromide of 1,2-di-(γ -pyridyl)-ethylene.

Anal. Calcd. for $C_{18}H_{11}N_7Br$: Br, 30.4. Found: Br, 30.2 (potentiometric titration).

The hydrobromide was triturated at room temperature with an excess of aqueous ammonia and the insoluble product filtered and recrystallized from water. M.p. and mixed m.p. with an authentic sample of 1,2-di-(γ -pyridyl)-ethylene, 155°.

1,2-Di-(γ -pyridyl)-ethane and Chloranil.—A solution was prepared of 0.56 g. (2.46 mmoles) of chloranil in 18 g. of hot

benzene and 0.42 g. (2.46 mmoles) of the ethane in 7 g. of hot benzene was added. Immediately, a brown-violet precipitate separated. After 2 hr. at room temperature, it was filtered, washed with benzene and dried; yield 1.0 g. The substance has no defined melting point; it decomposes gradually above 250°. The product peptizes in water; that the solution was colloidal was shown by the fact that addition of sodium or silver nitrate caused coagulation. This precipitate redispersed on washing to remove electrolyte. A water dispersion of the product was filtered and the filtrate was extracted with ether. The filtrate gave glistening black crystals on evaporation under the aspirator at 50°. Parr bomb analysis gave 30.0% chlorine, vs. 32.97% calculated for $C_{18}H_{11}O_2N_7Cl_4$, the molecular addition compound. On rewashing the product with ether, the chlorine fell to 28.6%. A second preparation was made as above, but with omission of the ether wash; black crystals, yield 100%. These were dried over calcium chloride and analyzed.

Anal. Calcd. for $C_{18}H_{11}O_2N_7Cl_4$: Cl, 32.97. Found: Cl, 32.1, 32.2.

Melting Point Diagram.—A sample of the pure ethylene obtained by the bromosuccinimide reaction was used as the standard for analysis of mixtures of ethane and ethylene by the absorption at 299 $m\mu$ of solutions in 95% ethanol. Beer's law was found to be valid. Assuming zero absorption at 299 $m\mu$ for the ethane, our best sample analyzed to 93.5%. Mixtures of this material with the pure ethylene were made, and melted. Both first liquefaction and final melting points were recorded. The samples were then cooled and remelted; the difference between initial and final values narrowed somewhat, due to the more intimate mixing in the melt. The remelt data are shown in Fig. 3; no eutectic point appears, and the two bases obviously form a continuous series of solid solutions. The point at 100% ethane is Thayer and Corson's value for their ethane prepared by catalytic hydrogenation of the ethylene.

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NEW HAVEN, CONNECTICUT

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

The Sorption of Vapors by Monolayers. V. The Differential Heats of Adsorption of *n*-Hexane on Stearic Acid Monolayers¹

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Adsorption of *n*-hexane on stearic acid monolayers has been calculated from measurements of surface pressure at 20°. Differential heats of sorption at 25° have been calculated from these data and data previously reported at 30°. On close packed monolayers the heat of sorption rises with increasing amounts of hexane sorbed reaching the heat of vaporization of hexane when the mole ratio of hexane to stearic acid is 0.5. On dilute stearic acid monolayers the initial heat of sorption is high but falls rapidly and, after passing through a minimum rises to approach the heat of vaporization when the surface is covered by a monolayer of hexane. On a clean water surface the heat of sorption is not significantly different from the heat of vaporization of *n*-hexane.

Very few measurements of adsorption have been made on plane surfaces where the area is known exactly and there are even fewer calculations of the heats of adsorption. Direct measurement of the quantity adsorbed is difficult because adsorption rarely exceeds 10 gibbs (10×10^{-10} mole/cm.^{2,3}). The amount of a solute or vapor adsorbed on a liquid surface can be calculated from the changes in

surface tension with concentration by means of the Gibbs equation. The calculation is straightforward for two component systems and Koenig⁴ has recently shown how to calculate adsorption from surface tension data in multicomponent systems.

We have recently⁵ calculated the adsorption of *n*-hexane on monolayers of stearic acid at 30°. This paper presents data on the same system at 20° together with heats of adsorption at 25° derived from the amounts adsorbed at 20 and 30°.

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³ R. B. Dean, *J. Phys. Colloid Chem.*, **55**, 611 (1951).

⁴ F. O. Koenig, "Calculation of Surface Concentrations from Surface Tension Data," Academic Press, Inc., New York, N. Y., in press.

⁵ K. E. Hayes and R. B. Dean, *THIS JOURNAL*, **73**, 5584 (1951).