heptane over the range of coverage investigated and the molar integral entropy of the adsorbed *n*-heptane decreases steadily with increasing coverage in a normal manner. The results for benzene are similar. The energy of adsorption of toluene is constant up to a coverage of 0.018 × 10^{16} molecules/cm.^{2}. It then falls by some 6 kcal./mole as the coverage is increased to 0.030 × 10^{16} molecules/cm.^{2}, and there is a corresponding rise in the molar entropy of the adsorbed material. Kemball and Rideal[5] suggested that at high coverages the adsorbed molecules were undergoing a change in orientation from "flat" to "vertical" adsorption and this was confirmed by the discovery of a small change in surface potential.[10] We believe that the fall in the energy and rise in the entropy of adsorption is consequent on this change of orientation. It is not likely to be due to the formation of a second layer because the area per molecule at the commencement of the change is 56 Å.^{2} while the area of a toluene molecule[5] is only about 37 Å.^{2}

Although the range Γ in Figs. 3 and 4 is small, we can say something about the limiting values of E_S and S_S as $\Gamma \rightarrow 0$ and $\Gamma \rightarrow \infty$ (assuming that Γ actually does approach infinity as $x \rightarrow 1$, as one expects below the critical temperature of the adsorbate on a non-porous adsorbent). As $\Gamma \rightarrow 0$, $E'_L - E_S \rightarrow$ finite and $S_S - S'_L \rightarrow +\infty$; as $\Gamma \rightarrow \infty$, $E'_L - E_S \rightarrow 0$ and $S_S - S'_L \rightarrow 0$.

The three substances show an interesting variation in freedom in the adsorbed state. Taking the vapor at one atmosphere pressure as the reference state, the experimental entropies of adsorption[11] of toluene, benzene and *n*-heptane are −51.3, −40.3 and −29.4 e.u. at coverages of 0.0135, 0.02 and 0.02 × 10^{16} molecules/cm.^{2}, respectively (roughly "corresponding states" judging from the energy and entropy curves). It is instructive to calculate the theoretical loss in entropy assuming that the molecules are forming a two-dimensional gas on the surface (neglecting interactions for simplicity) with free areas corresponding to the differences between the areas per molecule and the co-areas of the molecules as determined by Kemball and Rideal.[5] As the co-areas are 37, 35 and 33 Å.^{2}, respectively, the free areas are 37, 15 and 17 Å.^{2}. Using the usual equation for the three-dimensional translational entropy and the equation given by Kemball[6] for the two-dimensional translational entropy, the calculated losses are 19.6, 21.2 and 21.2 e.u., respectively. The fact that the experimental loss in entropy for *n*-heptane is only 8.2 e.u. greater than the value calculated on the model of the two-dimensional gas indicates that *n*-heptane has considerable freedom on the surface. Kemball[6] suggested that the adsorbed benzene might retain freedom to rotate in the plane of the ring but would lose the other two degrees of rotational freedom.[12] This model corresponds to a further loss of 16.9 e.u. making a total calculated loss of 38.1 e.u., which is to be compared with the experimental value of 40.3 e.u. The loss in entropy on adsorption of toluene is very much greater than the calculated value for the gaseous model. It is probable that the toluene is not freely mobile but it is not possible to suggest here what fraction of the loss of 51.3 e.u. is attributable to restriction of translation and what fraction to restriction of rotation (of the benzene ring and of the methyl group).

In this discussion we have ignored the small gain in entropy associated with the new vibrational degrees of freedom which must replace the lost degrees of translational and rotational freedom.

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[10] C. Kemball, *Proc. Roy. Soc.* (*London*), **201A**, 377 (1950).

[11] The values of s_G(1 atm.) − s'_L at $\bar{T}$ = 310.1°K. are 24.9, 23.3 and 24.4 e.u., respectively.

[12] See also J. W. Drenan and T. L. Hill, *J. Chem. Phys.*, **17**, 775 (1949).

Fischer Indole Syntheses with Polyphosphoric Acid

BY H. M. KISSMAN, D. W. FARNSWORTH AND B. WITKOP

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The successful application of polyphosphoric acid in cyclodehydration reactions[1,2] and Beckmann rearrangements[3] prompted us to try it in the Fischer indole synthesis especially in connection with those phenylhydrazones which are known to require drastic conditions for the elimination of ammonia and for indole ring closure.[4]

It was found that the use of polyphosphoric acid gave 2-phenylindole in good yields not only from acetophenone phenylhydrazone but also from a mixture of phenylhydrazine and acetophenone. A vigorous exothermic reaction and a color change from orange to dark brown took place when such a homogeneous mixture of phenylhydrazine, the ketone and polyphosphoric acid was heated to 120°. The indole could be isolated in fairly pure form by adding water to the reaction product.

An extension of this method to the preparation of other indole derivatives showed that it had fairly wide applicability. The aryl- and alkylsubstituted indoles shown in Table I were prepared from the corresponding ketones, phenylhydrazine and polyphosphoric acid. The reaction involving N-methylphenylhydrazine and acetophenone was carried out in order to see whether polyphosphoric acid could be used for the synthesis of N-substituted indoles. As expected, 1-methyl-2-phenylindole was obtained in good yield from this reaction. The use of isobutyrophenone and phenylhydrazine led to the isolation of 3,3-dimethyl-2-phenylindolenine showing that the polyphosphoric acid procedure could also be applied to the synthesis of indolenines.

In order to avoid tar formation it was very important, in all cases, to cool the reaction mixture immediately after the reaction had started. The maximum temperatures used in these reactions are shown in Table I. It is probable that the yields of some of these indole derivatives could be improved by changing these temperature conditions. The

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[1] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2962 (1950).

[2] E. C. Horning, J. Koo and G. N. Walker, *ibid.*, **73**, 5826 (1951).

[3] E. C. Horning and V. L. Stromberg, *ibid.*, **74**, 2680 (1952).

[4] R. L. Shriner, W. C. Ashley and E. Welch, *Org. Syntheses*, **22**, 98 (1942).

TABLE I

Ketone	Hydrazine	Indole	Reaction temp., °C.	Yield,[a] %	M.p.,[b] °C., cor.	Previous m.p., °C.
Acetophenone	α-Methyl-α-phenyl-	1-Methyl-2-phenyl-	100[c]	73[d]	100–101	100–101[e]
Acetophenone	Phenyl-	2-Phenyl-	180	76[f]	187–188	188–189[g]
p-Phenylacetophenone	Phenyl-	2,4′-Diphenyl-	185	63[h]	293–295[i]	297–298[j]
Propiophenone	Phenyl-	3-Methyl-2-phenyl-	170	58[k]	90– 92	91– 92[l]
Acetone	Phenyl-	2-Methyl-	203	60[k]	56– 59	60[m]
Methyl ethyl ketone	Phenyl-	2,3-Dimethyl-[n]	230[o]	68[p]	100–102	106[q]
Isobutyrophenone	Phenyl-	3,3-Dimethyl-2-phenyl indolenine[r]	155[c]	45	......	......

[a] Based on amount of ketone used. [b] All melting points are corrected (Kofler hot-stage). [c] Bath temperature. [d] Sublimed *in vacuo* and recrystallized from cyclohexane. [e] J. Degen, *Ann.*, **236**, 155 (1886). [f] Sublimed *in vacuo*. [g] See ref. (4) [h] Sublimed *in vacuo* and recrystallized from large amounts of ethyl acetate. [i] Microscopic slide, in sealed tube, m.p. 322–326°. [j] N. Buu-Hoi, N. Hoan, and R. Royer, *Bull. soc. chim. France*, [5] **17**, 489 (1950). [k] Sublimed twice *in vacuo*. [l] A. Collet, *Bull. soc. chim. France*, [3] 17, 74 (1897). [m] E. Fischer, *Ann.*, **236**, 127 (1886). [n] Best yields were obtained when phenylhydrazine and ketone were heated together on the steam-bath for a few minutes before the polyphosphoric acid was added. [o] The reaction is vigorous in spite of cooling but the mixture did not remain at this temperature for more than a few minutes. [p] Sublimed twice *in vacuo* and recrystallized from cyclohexane. [q] E. Fischer, *Ann.*, **236**, 129 (1886), obtained this melting point only after converting the indole to its N-nitroso derivative and reducing the latter after several recrystallizations. [r] See experimental.

use of temperatures much lower than those indicated (110–120°) led to the isolation of small quantities of basic by-products in the case of 2-phenylindole and 3-methyl-2-phenylindole; these substances have thus far not been identified.

The two benzyl ketones, desoxybenzoin and dibenzyl ketone, when allowed to react with polyphosphoric acid and phenylhydrazine, yielded intractable, highly colored, polymeric substances. These results could not be changed by using the separately prepared ketone phenylhydrazones or by varying the temperature conditions. Similar negative results were observed with phenylacetaldehyde and butyraldehyde, both as free aldehydes with phenylhydrazine or as phenylhydrazones. Therefore, it seems probable that polyphosphoric acid will be useless for the preparation of 2-unsubstituted indoles.

Experimental

General Method.—To a mixture of 0.05 mole of the ketone and 5 ml. of phenylhydrazine was added approximately 20 g. of polyphosphoric acid. The mixture was stirred with a thermometer and warmed gently on a steam- or oil-bath until a sudden rise of temperature indicated beginning of the reaction. By cooling the mixture externally with water at this point, the temperatures were maintained at the level shown in Table I. After the end of the reaction, 100 ml. of cold water was added to the cooled mixture which was then extracted thoroughly with ether. The combined, dried, ether extracts yielded the corresponding indoles which were purified by the methods indicated in Table I. Caution must be used in large scale runs because of the large amount of heat given off by the reaction mixture.

3,3-Dimethyl-2-phenylindolenine.—A homogeneous mixture of 14.2 g. of isobutyrophenone, 10.8 g. of phenylhydrazine and 30 g. of polyphosphoric acid was heated with vigorous stirring for a few minutes in an oil-bath at 155°. The color of the mixture changed from light yellow to dark brown. After cooling, there was added 150 ml. of ice-water and enough solid sodium carbonate to make the solution basic. Extraction with ether and removal of the solvent after drying yielded an oil which was distilled to give 9.5 g. (45%) of a slightly yellow liquid; b.p. 141–145° (1.5 mm.).

A **picrate**[5] melted at 153–155° after two recrystallizations from ethanol.

A **perchlorate** was prepared by the addition of 60% aqueous perchloric acid to a cold ethanolic solution of the indolenine. It melted at 194–195° after three recrystallizations from ethanol.

Anal. Calcd. for $C_{16}H_{16}NClO_4$: C, 59.72; H, 5.01; N, 4.53. Found: C, 59.65; H, 5.10; N, 4.45.

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[5] H. Leuchs, A. Heller and A. Hoffman, *Ber.*, **62**, 877 (1929), used zinc chloride for the preparation of this indolenine which they isolated by means of the picrate, m.p. 158–160°.

Heats of Fusion of Aliphatic Polyesters[1]

BY L. MANDELKERN, R. R. GARRETT AND P. J. FLORY

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An investigation,[2] the results of which were published several years ago, yielded discordant values for the heats of fusion of two linear polyesters, poly-(decamethylene adipate) and poly-(decamethylene sebacate). Heats of fusion calculated from the depressions of the melting points T_m caused by introduction of copolymerized units in the chains were substantially lower than those deduced from the dependence of T_m on chain length, and from that obtained in one instance from the lowering of T_m by diluents.[2] In more recent investigations[3,4] the latter method has been chosen in preference to measurements on copolymers principally because of the better definition of the melting points of the polymer–diluent mixtures, and also because of its wider applicability to polymers including those for which random alteration of some of the units, as by copolymerization, is impractical. Furthermore, the use of dilatometric methods permitting gradual melting over periods of several days yields more reliable melting points than the earlier micro method involving comparatively rapid heating of a small sample on the stage of a low power microscope.

In the light of these advances it seemed desirable to repeat the earlier determination of the heat of fusion of an aliphatic linear polyester by the diluent

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(1) This work was carried out at Cornell University as part of a research program supported by the Allegany Ballistics Laboratory, Cumberland, Md., an establishment owned by the United States Navy and operated by the Hercules Powder Company under Contract NOrd 10431.

(2) R. D. Evans, H. R. Mighton and P. J. Flory, THIS JOURNAL, **72**, 2018 (1950).

(3) P. J. Flory, L. Mandelkern and H. K. Hall, *ibid.*, **73**, 2532 (1951).

(4) L. Mandelkern and P. J. Flory, *ibid.*, **73**, 3206 (1951).