

from benzene-alcohol as colorless prisms melting at 202°, were isolated.

Anal. Found: C, 88.40; H, 5.64.

Summary

Dibiphenyleneethylene combines with ethylamine, methylamine and dimethylamine with facility at room temperature to give the corresponding substituted 1-aminodibiphenyleneethane derivatives. These products are quite labile and readily suffer dismutation to give fluorene and

the substituted 9-iminofluorenes. The addition of benzylamine and ammonia to the ethylenic linkage was relatively sluggish, and in the reaction involving the latter only the secondary products fluorene and 9-iminofluorene were obtained. With the possible exception of the recent work of Hickinbottom this appears to be the first case reported of the addition of amines to an unsaturated hydrocarbon containing an olefin double bond.

WASHINGTON, D. C.

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[CONTRIBUTION NO. 48 FROM THE CHEMICAL LABORATORY, UNIVERSITY OF UTAH]

The Direct Carboxylation of Carbon Compounds. III. The Free Energy of Benzoic Acid at 522°K.

BY W. D. BONNER AND C. R. KINNEY

Two papers dealing with the direct carboxylation of carbon compounds have been published from this Laboratory.¹ The theme of these two papers was that carboxylic acids may be produced directly from carbon compounds and carbon dioxide through the formation of an equilibrium gas mixture at high temperature and pressure. A catalyst always was present to facilitate the establishment of this equilibrium. The yields, except for one or two instances, were small. Furthermore, as stated in the first paper, an approximate calculation of the free energy showed that equilibrium probably lay well to the left in the reaction $C_6H_6 + CO_2 \rightarrow C_6H_5COOH$. Since, however, it did not seem possible to make a more precise free energy calculation, and as carboxylic acids certainly were obtained, albeit in small amounts, there seemed no reason for withholding the data from publication. Recently we have been able to calculate a more acceptable free energy value, and to arrive at a plausible reason for the observed formation of carboxylic acids.

Free Energy Calculations

For the reaction $C_6H_6(g) + CO_2(g) \rightarrow C_6H_5CO_2H(l)$ we find that $\Delta F_{298}^0 = 4300$ cal.² However, we wish to know ΔF^0 at 522°K.

The free energy of formation of benzene at any temperature T is given by the relation³

$$\Delta F_T^0 = 24,400 + 19.6T \ln T - 0.013T^2 - 87.0T$$

Therefore, $\Delta F_{522}^0 = 39,600$ cal. In a similar manner the free energy of formation of carbon dioxide at 522° is⁴ $\Delta F_{522}^0 = -94,263$. For benzoic acid a corresponding equation does not appear in the literature. Parks and Huffman⁵ give for the reaction

$7C + 3H_2 + O_2 \rightarrow C_6H_5CO_2H(l)$; $\Delta F_{298}^0 = -59,160$ ΔH_{298} (benzoic acid solid) as $-93,210$ cal. and the heat of fusion of benzoic acid at the melting point as 4140. Putting the general free energy equation into the form

$$\Delta F_T^0 = \Delta H^0 - \Delta C_P T \ln T + IT$$

we can evaluate these quantities one by one, and finally arrive at a value of ΔF_{522}^0 for benzoic acid. $\Delta C_P = C_P$ (products) $- C_P$ (reactants) = C_P (benzoic acid) $- C_P(7C, 3H_2, O_2)$. Using available heat capacity data⁶ we find ΔC_P between 25 and 249.2° to have an average value of 17.9 cal. per mole.

Using the value of ΔH_{298} (benzoic acid solid) already referred to, and assuming C_P (benzoic acid liquid) to be the same below as above the melting point, we calculate ΔH_{298} (benzoic acid liquid) = $-90,927$ calories. Then, since $\Delta H_T = \Delta H_0 + T\Delta C_P$, it follows that $\Delta H_0 = -90,927 - 17.9(298) = -96,261$ cal. The integration constant I , then is

$$I = \frac{\Delta F_{298}^0 - \Delta H_0 + \Delta C_P T \ln T}{T} = \frac{-59,160 + 96,261 + 17.9(298)(5.697)}{298} = 226.5$$

(1) Kinney and Langlois, *THIS JOURNAL*, **53**, 2189 (1931); Kinney and Ward, *ibid.*, **55**, 3796 (1933).

(2) Parks and Huffman, "Free Energies of Some Organic Compounds," A. C. S. Monograph No. 60, pp. 47 and 233.

(3) Parks and Huffman, *loc. cit.*, p. 93.

(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 576.

(5) Parks and Huffman, *loc. cit.*, pp. 134, 135.

(6) Parks and Huffman, *loc. cit.*, pp. 45, 46; "International Critical Tables," Vol. V, pp. 104, 110.

Substituting these and the value of ΔF_{298}^0 into the free energy equation we get ΔF_{522}^0 (benzoic acid) = -36,491 cal. From this it follows that the free energy of formation of benzoic acid from benzene and carbon dioxide at 522°K. is 18,172 cal. The equilibrium constant for this reaction is calculated, from the relationship $-\Delta F^0 = RT \ln K$, to be $K = 10^{-7.63}$.

It can be shown readily that this value will not be much affected by an increase of pressure of the order of 35 atmospheres. It is evident that in the reactions studied by Kinney and his students, the equilibrium amounts of carboxylic acids cannot account for the quantities actually found. The most plausible explanation, it seems to us, is that the zinc oxide of their oxide catalyst was slowly converted into the zinc salt of a carboxylic acid, and in this way appreciable amounts were built up in their apparatus. This

would account also for the observation that fresh catalysts were always most effective and that the catalyst became almost inactive by the third usage.

This emphasizes the fact that catalysts may not always be purely catalysts, but that small amounts of products may result from direct chemical action with the catalyst or with one of its constituents. In such cases free energy data if available are of great value.

We acknowledge indebtedness to Professor George S. Parks for criticizing the preliminary calculations, and to Dr. Lyman G. Bonner for rechecking the final ones. The latter also has made a precise calculation of the free energy of benzoic acid at the boiling point, using complete heat capacity equations. This calculation, however, differs from ours by less than 0.5%.

SALT LAKE CITY, UTAH

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[CONTRIBUTION FROM THE UNIVERSITY OF AKRON]

Binary Systems of *p*-Dichlorobenzene with Diphenyl, Naphthalene and Triphenylmethane

BY ROSS E. MORRIS AND WALTER A. COOK

Schröder¹ some years ago showed that *p*-dibromobenzene forms an almost perfect solution with benzene. The purpose of this investigation was to find the nature of solutions of *p*-dichlorobenzene with various aromatic hydrocarbons. Those chosen were diphenyl, naphthalene and triphenylmethane. These solutions have not been previously investigated.

In the following report the solubilities, eutectic temperatures and eutectic compositions are compared with values calculated for perfect solutions from the equation given by Washburn²

$$dT_f = \frac{RT_f^2}{\Delta H_f} \frac{dN}{N}$$

where T_f is the freezing point of the solution, ΔH_f is the heat of fusion of the crystals separating from the solution at the freezing point, R is the gas constant and N is the mole fraction of the component which crystallizes at the freezing point. The values for ΔH_f are given in Table I.

Materials.—Commercial naphthalene and *p*-dichlorobenzene were purified by distillation until

(1) Schröder, *Z. physik. Chem.*, **11**, 449 (1893).

(2) Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., Inc., New York City, 1921 p 202.

TABLE I
HEAT OF FUSION ΔH_f
G. cal./mole

		Ref.
<i>p</i> -Dichlorobenzene	$-10,250 + 94.07T - 0.1511T^2$	3
Diphenyl	$-11,240 + 112.8T - 0.2835T^2 + 0.0002568T^3$	4
Naphthalene	$+4265 - 26.31T + 0.1525T^2 - 0.0002140T^3$	4
Triphenylmethane	$-9230 + 66.35T - 0.07324T^2$	4

no further changes in melting points were observed. Eastman c. p. grade of diphenyl and triphenylmethane were purified by recrystallization, the former from alcohol and the latter from acetone, and dried *in vacuo*. The melting points of the purified materials are compared with the "International Critical Tables" values in Table II.

The agreement in melting points is good except in the case of triphenylmethane. The "I. C. T." value is undoubtedly too low for this compound.

(3) Calculated from specific heat and heat of fusion data given in "International Critical Tables," Vol. V, p. 132.

(4) Calculated from specific heat and heat of fusion data given by Spaght, Thomas and Parks [*J. Phys. Chem.*, **36**, 882 (1932)].