ends of the reaction tube, the pressure which they recorded was only approximately that at the ends of the tube.

In making a run, the vapor from a mixture of the isomers in the liquid state contained in a glass storage bulb was allowed to flow through the reaction tube at a definite rate, controlled by a Fowler[2] gas leak and a streaming manometer. The reaction products were frozen out in a liquid air trap, from which they could be removed for analysis. The composition of the samples used in the runs was varied sufficiently so that the equilibrium was approached from both sides.

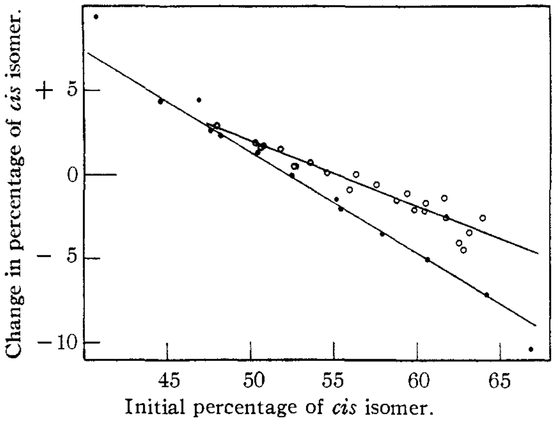

Fig. 1.—●, 975°; ○, 825°.

The two lines in Fig. 1 were obtained by plotting the change in the percentage of the *cis* isomer during a run against the initial percentage of that isomer. The composition corresponding to the point of zero change is the composition of the equilibrium mixture. The second and third columns of Table I give the average values of the pressures at the ends of the reaction tube as measured by the manometers. The values for the composition of the thermal equilibrium mixtures given in the next column are from Fig. 1.

Table I

Temp., °C.	Pressure, mm. Hg Input	Pressure, mm. Hg Output	% *cis* at equil.
975	7.5	0.30	52.3
825	11.2	.34	55.1

In calculating ΔH, the heat of transition, Olson and Maroney[1] used the approximate equation $N_{trans}/N_{cis} = e^{-\Delta H/RT}$ because the possible errors in the equilibrium constants were so large compared to the change in the equilibrium constant for the fifty-degree change in temperature. If we now combine the present equilibrium constants with those given by Olson and Maroney and use the exact equation

$$\Delta H = \log \frac{K_1}{K_2} \times 4.58 \frac{T_1T_2}{\Delta T}, \text{ we get}$$

$$\Delta H_{300-975^\circ} = 725 \text{ cal.}, \quad \Delta H_{350-875^\circ} = 510 \text{ cal.}$$

the average of which agrees almost exactly with the value $\Delta H_{300^\circ} = 600$ cal. given by Ebert and Büll.[3]

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(2) R. D. Fowler, *Rev. Sci. Inst.*, **6**, 26 (1935).

(3) Ebert and Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

Berkeley, California Received September 23, 1935

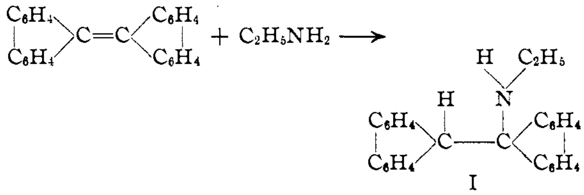
[Contribution from the Fertilizer Investigations Unit of the Bureau of Chemistry and Soils, U. S. Department of Agriculture]

Interaction of Amines and Ammonia with Dibiphenyleneethylene

By L. A. Pinck and Guido E. Hilbert

With the aim of obtaining more information that might aid in elucidating the mechanism of the interaction between 9-fluorylamine and dibiphenyleneethylene in liquid ammonia which gives as end-products 9-iminofluorene and dibiphenyleneethane,[1] and in order to test the suspected similarity of the double bond in dibiphenyleneethylene to an ethylenic linkage adjacent to an activating group, as carbonyl or cyano,[2] we have been led to investigate the action of amines on dibiphenyleneethylene.

It has now been found that dibiphenyleneethylene combines easily at room temperature with ethylamine, methylamine or dimethylamine to give 1-ethylamino (I), 1-methylamino (II) and 1-dimethylaminodibiphenyleneethane, respectively.



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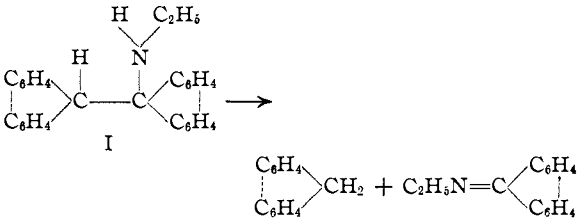
(1) Pinck and Hilbert, This Journal, **54**, 710 (1932).

(2) Lapworth and McRae, *J. Chem. Soc.*, **121**, 2741 (1922), and Kolker and Lapworth, *ibid.*, **127**, 307 (1925), have suggested that the properties of an ethylenic linkage, which is in the α,β-position with respect to a carbonyl group, are intermediate to those of a normal ethylenic linkage and those of the carbonyl group.

As the rate of addition of these amines to the double bond is relatively rapid, the slow side reactions which occur subsequent to the formation of the amine, are of minor significance and depress the yield of the primary product only slightly below that required by theory. However, in the interaction of benzylamine or ammonia with dibiphenyleneethylene the rate of addition of the base to the unsaturated grouping is so slow that the secondary reactions assume a major role. These reactions are favored by elevated temperatures and 1-benzylaminodibiphenyleneethane (III) can be prepared in fair yield only by carrying out the reaction (several months for completion) at room temperature. When ammonia is used as the basic reactant, only secondary products can be isolated from the reaction mixture. In contrast to the behavior of the above amines, diethylamine, triphenylmethylamine or aniline do not react under conditions which are generally more favorable than those used for the other amines. The comparative data obtained indicate that the rate of addition of amines to dibiphenyleneethylene is in the order $CH_3NH_2 > C_2H_5NH_2 > (CH_3)_2NH > C_6H_5CH_2NH_2 > NH_3 > (C_2H_5)_2NH$ or $C_6H_5NH_2$. Such data as are available in the literature point to the same order of addition of amines to α,β-unsaturated acids. It is interesting to note that although II readily forms an acetyl derivative, I and III fail to react when subjected to the usual acetylation procedures. All three amines however interact with nitrous acid to give nitroso derivatives. Additional evidence indicating the presence of the –NH– grouping in I, II and III was secured by Dr. Wulf and Mr. Liddel of the spectroscopic section of this Laboratory by a study of the infra-red absorption spectra in the region 1.65–1.45 μ; the molal absorption area (cm.$^{-1}$) was found to be 7, 9 and 8, respectively. The –NH– absorption per molecule is thus somewhat lower than has yet been experienced with the rather large and varied group of organic –NH– compounds which they have investigated.[3]

These amines are quite sensitive to thermal conditions and the nature of the decomposition is influenced by the character of the medium in which they are dissolved. In alcohol at 100° the dismutation of I yields fluorene and 9-ethylimino-fluorene exclusively. But in ethylamine a different type of scission leading to the formation of dibiphenyleneethane and ethylideneimide also occurs. Because of the high temperature and the length of time required to effect a reaction between ammonia and dibiphenyleneethylene, the primary product formed, 1-aminodibiphenylenethane, does not survive and only the secondary products, fluorene and 9-iminofluorene are found in the reaction mixture.



Although there are numerous examples of the facile combination of ammonia or amines with unsaturated acids or related compounds in which the double bond is in the α,β-position to form the respective β-amino or β-substituted amino acids,[4] the only investigation other than the work reported here on the combination of amines with the ethylenic linkage of unsaturated hydrocarbons appears to be that of Hickinbottom.[5,6] The employment of a promoter (amine hydrochloride) in the examples studied by Hickinbottom obscures the mechanism of the reaction and it is by no means certain, in view of the type of catalyst used, that the reaction product was not formed indirectly.[7] On the other hand, the combination of amines with dibiphenyleneethylene is effected in the absence of any promoter and would thus seem to allow of no other interpretation than that of direct addition of the amine to the ethylenic linkage.

Although general experience in the past[8] would have seemed to indicate that there is an abrupt change in the reactivity of ethylenic linkages in unsaturated hydrocarbons as compared to those in unsaturated α-carbonyl compounds toward

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[3] Liddel and Wulf, THIS JOURNAL, **55**, 3574 (1933); Wulf and Liddel, *ibid.*, **57**, 1464 (1935).

[4] See Phillippi and Galter [*Monatsh.*, **51**, 253 (1929)] for an extensive survey of this subject.

[5] Hickinbottom, *J. Chem. Soc.*, 2646 (1932): 319 and 1981 (1934).

[6] It is interesting to note that calculations assuming the validity of the Nernst approximation formula indicate that the reaction of ethylene and ammonia to give ethylamine is thermodynamically possible.

[7] A discussion of the nature of the reaction was postponed by Hickinbottom in order to test experimentally the various hypotheses that might be proposed to account for the reaction. As the aromatic amine hydrochlorides, which were used as catalysts, are appreciably dissociated at the temperatures at which these reactions were carried out, it seems to us quite possible that the formation of the amines was dependent on the prior addition of hydrogen chloride to the double bond.

[8] Lapworth and McRae *J. Chem. Soc.*, **121**, 2741 (1922); Kolker and Lapworth, *ibid.*, **127**, 307 (1925).

certain reagents as amines, hydrogen cyanide, diethyl malonate, etc., our work shows that the properties of the double bonds, even in unsaturated hydrocarbons, when the appropriate groups are attached, can approach in similarity those of the unsaturated linkage in the grouping —CH=CHCO—. The natural inference is that the electronic configuration of the double bond in dibiphenyleneethylene is more like that of the ethylenic linkage with an adjacent carbonyl group than that of the normal type in ethylene. This suggests the possible interaction of dibiphenyleneethylene with other reagents that are generally considered to be specific for compounds containing the group —CH=CHCO—. Moreover, in view of the activating influence of the biphenylene group upon a double bond, one might expect a like effect upon the methylene group in fluorene and its derivatives and this seems to be substantiated by the remarkable parallelism of many of its reactions, although the rates are much slower, with those of the methylene group in a compound such as diethyl malonate.

We wish to express our appreciation to Dr. R. T. Milner and Mrs. M. S. Sherman for the recorded microanalyses.

Experimental

Interaction of Dibiphenyleneethylene with Ammonia.—A mixture of 1 g. of dibiphenyleneethylene and 15 cc. of liquid ammonia was heated in a sealed tube at 65° for three weeks. At the end of this time it was apparent that the red ethylene compound was completely altered. After opening the tube, the ammonia was removed and the residue triturated with dry ether. The fraction insoluble in ether weighed 0.5 g. and melted at 295°; it was crystallized from acetone and separated as colorless prisms; m. p. 300°.[9] Treatment of the ether extract with dry hydrogen chloride precipitated the orange colored hydrochloride of 9-iminofluorene, yield 0.40 g.; m. p. 303° (dec.).[10] The hydrochloride was converted into the free base which was crystallized from hexane; yellow needles; m. p. 123°; m. p. when mixed with 9-iminofluorene unchanged.

Anal. Calcd. for $C_{13}H_9N$: C, 87.11; H, 5.06; N, 7.82. Found: C, 87.22; H, 5.25; N, 7.81.

The ether filtrate from 9-iminofluorene hydrochloride was concentrated to dryness; 0.07 g. of fluorene was removed by sublimation; m. p. 114°; the m. p. when mixed with fluorene was unchanged.

1-Ethylaminodiphenyleneethane (I).—Two grams of dibiphenyleneethylene in 10 cc. of ethylamine reacted completely in two days when heated at 65°. Excess ethylamine was removed by distillation, the residue dissolved in dry benzene and 1-ethylaminodibiphenyleneethane precipitated as the hydrochloride; m. p. 210–215° (dec.). This was converted to the free base, which was crystallized from a benzene–alcohol solution; it separated as colorless prisms melting at 165°; yield 65% of the theoretical. It is soluble in benzene, hot hexane and slightly soluble in alcohol.

Anal. Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75; mol. wt., 373. Found: C, 89.86; H, 6.39; N, 3.73; mol. wt., 369.

From the benzene–hydrogen chloride filtrate there were isolated small amounts of the secondary products fluorene (sublimation) and dibiphenyleneethane. As is shown below these products originated from a relatively slow degradation of I in ethylamine and obviously for the preparation of it in good yield excessive heating and a delay in working up the reaction mixture is to be avoided.

The picrate crystallized from an alcoholic acetone solution; yellow diamond-shaped prisms; m. p. 228° (dec.).

Anal. Calcd. for $C_{34}H_{26}N_4O_7$: C, 67.76; H, 4.35; N, 9.30. Found: C, 67.86; H, 4.50; N, 9.19.

The nitroso derivative was prepared by treating a solution of the amine in acetic acid with an aqueous solution of sodium nitrite. It separated from an acetone–alcohol solution as pale yellow rhombic crystals melting at 217°; very soluble in acetone and slightly soluble in alcohol and ether; the yield was practically quantitative.

Anal. Calcd. for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.98; H, 5.47; N, 6.98.

This, as well as the other nitroso derivatives, did not respond to the Liebermann nitrosoamine test, which is based on the nitrous acid formed in the scission of the —N—N— linkage. The negative test in these particular compounds may be accounted for by the preferential rupture of the —C—N— linkage[11] to form methyldiazonium hydroxide, which would decompose and liberate nitrogen. It is noteworthy that the nitrosoamine when treated with concentrated sulfuric acid immediately generated considerable gas. When warmed, the brown colored acid mixture turned to a red solution and this on dilution with water deposited red flocks suggestive of dibiphenyleneethylene. An oxdiazolidine structure has also been considered for the nitroso compound but this possibility was definitely excluded since a carbon tetrachloride solution showed no —NH— absorption in the region 1.65–145 μ.

Dismutation of 1-Ethylaminodibiphenyleneethane.—A solution of 2 g. of 1-ethylaminodibiphenyleneethane in 20 cc. of absolute ethyl alcohol was heated at 100° for ten days. After concentrating the alcoholic solution, the yellow sirupy residue was dissolved in hexane and treated with dry hydrogen chloride, yielding 0.90 g. of a pale peach-colored precipitate. The residue obtained by concentrating the filtrate was sublimed *in vacuo;* yield 0.81 g. of a yellow colored sublimate, that consisted mainly of fluorene contaminated with some fluorenone, which was probably formed by the hydrolysis of a portion of the imide. The fluorenone was separated from fluorene by converting it to the difficultly soluble fluorenone ketazine (0.10 g.; m. p. 267°).[12] Fluorene was recovered from the

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[9] Evidence concerning the structure and the mechanism of the formation of this compound is the subject of a further investigation.

[10] All melting points are corrected.

[11] Kharasch and Howard [This Journal, **56**, 1370 (1934)] showed that triphenylmethylamine is hydrolyzed by acid.

[12] Taipale, *Ber.*, **63**, 243 (1930).

filtrate and identified; yield, 0.67 g. The hydrochlorides representing the basic fraction were treated with liquid ammonia and the mixture concentrated. The residue was extracted with hexane and the extract concentrated to a yellow sirup (9-ethyliminofluorene). This was hydrolyzed to fluorenone; yield 0.31 g. In another experiment the amine (0.5 g.) was degraded and the 9-ethyliminofluorene isolated as the picrate by adding an alcoholic solution of picric acid to the reaction mixture; yield 0.20 g.; m. p. 204° (dec.), m. p. 205° (dec.) when mixed with the specimen obtained below.

Anal. Calcd. for $C_{21}H_{16}N_4O_7$: C, 57.79; H, 3.70; N, 12.86. Found: C, 58.03; H, 3.81; N, 12.94.

The decomposition of 1-ethylaminodibiphenyleneethane was also studied in ethylamine in order to gain information concerning the origin of the fluorene and dibiphenyleneethane that were isolated as by-products in the interaction of ethylamine with dibiphenyleneethylene. 1-Ethylaminodibiphenyleneethane (1 g.) was heated in ethylamine (15 cc.) in a sealed tube at 85° for several days. The ethylamine was removed from the reaction mixture, the residue dissolved in benzene and the bases separated by means of hydrogen chloride. From the filtrate there was isolated 0.18 g. of dibiphenyleneethane and 0.15 g. of fluorene. Attempts to ascertain the nature of the basic fragment resulting simultaneously with dibiphenyleneethane were not successful and this is not surprising, since the initial product to be expected, ethylideneimine[13] would subsequently either suffer polymerization or react with the medium to yield ethylideneethylamine.

9-Ethyliminofluorene was prepared for purposes of comparison with the product obtained above. A solution of 1.3 g. of 9-iminofluorene[14] and 20 cc. of ethylamine was heated at 55° for eighteen hours and gradually assumed a pale green color. The ethylamine was removed and the yellow sirup was placed in an evacuated desiccator containing sulfuric acid; it did not crystallize and slowly developed a greenish color. It was converted to the *picrate* which separated from a solution of nitrobenzene and alcohol as orange needles; m. p. 206° (dec.).

Anal. Calcd. for $C_{21}H_{16}N_4O_7$: C, 57.79; H, 3.70; N, 12.86. Found: C, 58.00; H, 3.90; N, 12.86.

The low yield, 0.57 g., of the imide picrate is significant and may be accounted for by isomerization of the imide during its preparation as it is a prototropic system.[15]

1-Methylaminodibiphenyleneethane.—The reaction between dibiphenyleneethylene (2 g.) and methylamine at room temperature was complete in one day. The reaction product was crystallized from hexane; yield 1.55 g.; m. p. 151°.

Anal. Calcd. for $C_{27}H_{21}N$: C, 90.22; H, 5.89; N, 3.90. Found: C, 90.41; H, 5.92; N, 3.98.

The acetyl derivative separated as colorless plates from alcohol; m. p. 232°.

Anal. Calcd. for $C_{29}H_{23}NO$: C, 86.75; H, 5.78; N, 3.49. Found: C, 86.66; H, 5.80; N, 3.40.

The nitroso derivative crystallized from alcohol as long prisms melting at 203°. It was soluble in hot carbon tetrachloride and separated with one molecule of solvent of crystallization.

Anal. Calcd. for $C_{27}H_{20}N_2O \cdot CCl_4$: CCl_4, 28.38. Found: CCl_4 (loss *in vacuo*), 28.65. Calcd. for $C_{27}H_{20}N_2O$: C, 83.47; H, 5.19; N, 7.22. Found: C, 83.48; H, 5.20; N, 7.39.

1-Dimethylaminodibiphenyleneethane crystallized from a solution of alcohol containing 20% benzene as colorless distorted hexahedra; m. p. 215° (dec., red liquid).

Anal. Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 89.88; H, 6.44; N, 3.85.

Reaction of Dibiphenyleneethylene with Benzylamine.—A mixture of 5 g. of dibiphenyleneethylene and 20 cc. of benzylamine was kept in a sealed tube for about six months, when it was evident that no more of the unsaturated hydrocarbon was present. The supernatant liquid was decanted from the precipitated dibiphenyleneethane (0.80 g.) and transferred into one leg of a two-legged tube. The benzylamine was distilled under diminished pressure from one portion of the tube which was immersed in boiling water, to the other which was cooled by an acetone–carbon dioxide mixture. The residue was triturated with a small quantity of cold alcohol and dried; yield 4.62 g. 1-Benzylaminodibiphenyleneethane was purified by crystallizing first from a solution of 1 part benzene and 4 parts alcohol and then from propyl alcohol; short stout prisms; m. p. 168°.

Anal. Calcd. for $C_{33}H_{25}N$: C, 91.04; H, 5.79; N, 3.17. Found: C, 91.00; H, 5.84; N, 3.27.

The hydrochloride could be recrystallized from benzene; m. p. 215–218°.

Anal. Calcd. for $C_{33}H_{26}NCl$: N, 2.97; Cl, 7.51. Found: N, 3.04; Cl, 7.40.

The nitroso derivative separated from a solution of acetone and alcohol as stubby prisms melting at 217–218°.

Anal. Calcd. for $C_{33}H_{24}N_2O$: C, 85.31; H, 5.21; N, 6.03. Found: C, 85.68; H, 5.42; N, 6.28.

An attempt to prepare the methiodide was unsuccessful.

When a solution of dibiphenyleneethylene (5 g.) in benzylamine (10 cc.) was heated at 100° the reaction was completed in six days. From the reaction mixture there were isolated dibiphenyleneethane (2.2 g.), fluorene (0.05 g.), an unidentified hydrocarbon (1.0 g., small colorless plates from xylene; m. p. 318° (decomp. to red melt). *Anal.* Found: C, 94.43; H, 5.49), 1-benzylaminodibiphenyleneethane and an unidentified base[16] crystallized from alcohol; m. p. 90°.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.43; H, 7.33; N, 9.24. Found: C, 83.67; H, 7.24; N, 9.19. Hydrochloride, m. p. 212°. *Anal.* Calcd. for $C_{21}H_{24}N_2Cl_2$: C, 67.19; H, 6.45; N, 7.47. Found: C, 67.23; H, 6.42; N, 7.27.

Dismutation of 1-benzylaminodibiphenyleneethane was effected by heating 1 g. in 20 cc. of absolute ethyl alcohol in a sealed tube at 100° for ten days. Fluorene (0.25 g.), small quantities of fluorenone and benzaldehyde[17] and a few milligrams of an unidentified product, which separated

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[13] Strain, THIS JOURNAL, **54**, 1221 (1932).

[14] Pinck and Hilbert, *ibid.*, **56**, 490 (1934).

[15] Ingold and Wilson, *J. Chem. Soc.* 1493 (1933).

[16] Compare with the benzyldiaminostilbene of Japp and Moir, *J. Chem. Soc.*, **77**, 608 (1900).

[17] Fluorenone and benzaldehyde were formed by hydrolysis of the basic fraction indicative that some isomerization of 9-benzyliminofluorene had taken place; see Ingold and Wilson, *J. Chem. Soc.*, 1493 (1933).

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. Received August 8, 1935

[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 $C_6H_6 + CO_2 \longrightarrow C_6H_5COOH$. 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 $C_6H_6(g) + CO_2(g) \longrightarrow C_6H_5CO_2H(l)$ we find that $\Delta F^0_{298} = 4300$ 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 relation[3]

$$\Delta F^0_T = 24{,}400 + 19.6T \ln T - 0.013T^2 - 87.0T$$

Therefore, $\Delta F^0_{522} = 39{,}600$ cal. In a similar manner the free energy of formation of carbon dioxide at 522° is[4] $\Delta F^0_{522} = -94{,}263$. For benzoic acid a corresponding equation does not appear in the literature. Parks and Huffman[5] give for the reaction

$$7C + 3H_2 + O_2 \longrightarrow C_6H_5CO_2H(l);\quad \Delta F^0_{298} = -59{,}160$$

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

$$\Delta F^0_T = \Delta H^0 - \Delta C_P\, T \ln T + IT$$

we can evaluate these quantities one by one, and finally arrive at a value of ΔF^0_{522} 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 data[6] 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

$$I = \frac{\Delta F^0_{98} - \Delta H_0 + \Delta C_P T \ln T}{T} = \frac{-59{,}160 + 96{,}261 + 17.9(298)\,(5.697)}{298} = 226.5$$

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[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.