hardly have taken place to the same extent in the tubes starting from the opposite sides of the reaction. The same constant could hardly have been obtained from both sides of the reaction. The difficulty of preparing the tubes containing isobutene as a starting material is an unavoidable contributing factor. Less agreement was obtained in the values approaching the equilibrium from this direction. The largest factor in experimental error is attributed to the free space in the reaction tubes. Unsuccessful attempts were made to determine the amount of unsaturate in this space. The space was kept as small as possible and still prevent explosions. The method of analysis determines the entire unsaturated material in the tube and not in the liquid phase only. The results reported by this method have this inherent small error.

Additional work upon triethylcarbinol and tripropylcarbinol, as yet incomplete, indicates that the constant for trimethylcarbinol is approximately one hundred times as large as that for triethylcarbinol, while the constant for tripropylcarbinol is approximately three times that of the triethylcarbinol.

Summary

1. The equilibrium constant for the hydration of isobutene at 100° is 3.8 × 10.
2. While the constants were obtained, by both hydration and dehydration measurements, in good agreement, the method is subject to an experimental error which cannot be minimized.
3. Preliminary measurements have been made upon triethyl and tripropyl carbinols. The percentage dehydration of tripropylcarbinol is between that of trimethyl- and triethylcarbinols.

EMORY UNIVERSITY, GEORGIA RECEIVED MAY 12, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Association of Benzoic Acid in Benzene

BY F. T. WALL AND P. E. ROUSE, JR.[1]

Several different methods have been used to study association in solution.[2] Among them is the investigation of the distribution of a solute between immiscible solvents. For example, the distribution of benzoic acid between water and benzene is found to be in agreement with the idea that benzoic acid is dimerized in benzene and exists as a monomer in water.[3] From a measurement of the dependence of such a distribution coefficient on temperature, Hendrixson[4] obtained a measure of the heat of dissociation of the benzoic acid dimer. This method, however, was subject to some uncertainties due to the mutual solubilities of the solvents.

Another method, which was employed by Lassettre and Dickinson,[5] involved the distribution of a volatile solvent between two solutions of (practically) non-volatile solutes. In the investigation here reported, a method similar to that of Lassettre and Dickinson was used to study the association of benzoic acid in benzene. The chemical reaction involved is

$$(C_6H_5COOH)_2 \leftrightarrows 2C_6H_5COOH \qquad (1)$$

Apparatus.—The isopiestic apparatus used was similar in design to that of Lassettre and Dickinson.[5] Two solution bulbs were joined by an inverted U-tube and each was provided with a calibrated side arm for volume measurements. When the apparatus was in a horizontal position, the solutions rested in the bulbs mentioned, but when the apparatus was rotated through ninety degrees, the solutions drained into their respective side arms.

To speed up the rate of distillation it was necessary, as far as possible, to remove all air from the system. The apparatus was evacuated by pumping through a tube attached to the U-tube, the gases passing through a mercury trap before entering the vacuum line. The mercury trap was present to make visible the rate of evacuation and to prevent too rapid ebullition of solvent with consequent danger of mixing the solutions.

The system was attached to the vacuum line by neoprene tubing which was closed by a heavy brass clamp that also served to regulate the rate of evacuation. Neoprene tubing and a brass clamp were used in place of a glass stopcock because solvent vapor was found to attack the stopcock grease.

Calibration of the graduated side-arms was carried out by weighing the apparatus alone and then with varying amounts of mercury in one arm or the other. In order that the volume readings could be applied to benzene solutions,

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(1) Du Pont fellow in Chemistry, 1940–1941.

(2) See E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937), for a discussion.

(3) Creighton, *J. Franklin Inst.*, **180**, 63 (1915); Nernst, *Z. physik. Chem.*, **8**, 110 (1891).

(4) W. S. Hendrixson, *Z. anorg. Chem.*, **13**, 73 (1897).

(5) E. N. Lassettre and R. G. Dickinson, THIS JOURNAL, **61**, 54 (1939).

it was necessary to apply a correction because of the difference between the benzene and mercury menisci.

Since it was essential that both solutions have the same temperature, a special thermostat was constructed with the needs of this experiment in mind. The thermostat consisted of a heavy gage copper box 12" wide, 20" deep and 22" long provided with a 4" × 16" plate glass window sealed into slots at one end by means of aquarium cement. The copper box was surrounded by one-half inch of asbestos and around it was built a box of one-inch redwood to give it strength. The window was provided with an insulated door which was kept closed except during readings.

The thermostat was also provided with an insulated top. Suspended from the end of the top opposite the window was a turbine type stirrer which stirred the water in the thermostat quite vigorously. The isopiestic apparatus previously described was held in place by a brass Bunsen clamp attached to a horizontal axle across the width of the tank near the window end. The axle was connected through an eccentric mechanism and speed reducer to a motor which was mounted on top of the thermostat and which also ran the stirrer. By means of this device the glass apparatus was oscillated slowly through a few degrees from its normal horizontal position to eliminate surface concentration effects during experimental runs. To read volumes, the apparatus was turned about the axle to a vertical position with the graduated arms just opposite the window.

The temperature of the thermostat was controlled by means of a large mercury thermal regulator provided with a thyratron relay. Heat was supplied by electric light bulbs arranged as symmetrically as possible to minimize transverse temperature gradients. As pointed out by Lassettre and Dickinson,[5] small temperature gradients can produce an appreciable effect on the distribution of solvent.

Materials.—The solvent was Merck reagent thiophene-free benzene which was refluxed over metallic sodium for twenty-four hours and then distilled into a storage flask containing sodium. Eastman Kodak Co. phenanthrene melting at 98.5–99.5° was used for a standard substance. Because of its smaller vapor pressure, phenanthrene was found more desirable as a standard than naphthalene. The benzoic acid was recrystallized several times from water and then dried in a vacuum oven at 80° for fifteen hours. The melting point of the substance after this purification was 122°.

Procedure.—Accurately weighed amounts of benzoic acid and phenanthrene were dissolved in benzene and introduced into the apparatus with excess of solvent. Air and excess solvent were then removed by successive pumpings, ample time being allowed between pumpings for dissolved air to escape from the solutions. To ensure complete removal of air, the apparatus was kept in a warm bath prior to pumping.

The solutions were allowed to come to equilibrium at each of three temperatures in the neighborhood of 32, 44 and 56°. During the runs, volume readings were made two or three times each day to follow the progress of the distillation. As equilibrium was approached, the distillation slowed up appreciably. To speed the procedure, pieces of ice were held momentarily to the side of the apparatus toward which distillation was taking place. The system was always permitted to approach equilibrium from both sides, ice being used to transfer a slight excess of solvent to one side as necessary. The volume readings obtained by nearing equilibrium from opposite sides generally agreed within 0.02 ml., the uncertainty of a reading being 0.01 ml. The averages of such readings were taken as equilibrium values. The total time required to obtain such equilibrium volumes at the lowest temperature varied from four to six days. At higher temperatures the time was appreciably reduced.

The results of the experimental observations are summarized in Table I. The volumes given there are the

TABLE I

Expt.	Temp., °C.	$C_{14}H_{10}$, g.	$C_{14}H_{10}$ soln., ml.	C_6H_5COOH, g.	C_6H_5COOH soln., ml.	M_2'	σ	$K \times 10$
1	32.09	0.4475	23.79	0.6524	27.12	229.2	0.0656	1.81
2	32.09	.2426	25.88	.3238	27.48	224.6	.0877	1.63
3	32.68	.6100	20.36	.7775	20.20	231.0	.0572	2.19
4	32.68	.3845	18.20	.4915	18.24	228.7	.0681	2.20
5	32.70	.5663	21.20	.6735	19.69	230.0	.0618	2.28
6	32.70	.4910	23.33	.6652	24.92	227.4	.0741	2.59
7	32.73	.1112	15.10	.1427	15.81	218.8	.1164	2.27
1	43.75	0.4475	23.80	0.6524	27.79	223.6	0.0924	3.62
2	43.48	.2426	25.88	.3238	28.22	218.6	.1172	2.92
3	43.93	.6100	20.43	.7775	20.62	227.0	.0760	3.86
4	43.93	.3845	18.28	.4915	18.56	225.6	.0829	3.25
5	43.90	.5663	21.28	.6735	20.11	226.0	.0809	3.91
6	43.90	.4910	23.44	.6652	25.37	224.3	.0887	3.71
7	43.90	.1112	15.07	.1427	16.25	212.4	.1498	3.80
1	56.09	0.4475	23.87	0.6524	28.46	218.9	0.1157	5.68
2	56.10	.2426	25.74	.3238	29.14	210.5	.1604	5.58
3	56.82	.6100	20.44	.7775	21.16	221.0	.1050	7.41
4	56.82	.3845	18.31	.4915	18.99	220.9	.1058	5.31
5	56.82	.5663	21.29	.6735	20.61	220.4	.1082	7.03
6	56.82	.4910	23.45	.6652	25.94	219.5	.1130	6.05
7	56.80	.1112	14.94	.1427	16.62	203.4	.2006	7.00

equilibrium volumes of the benzoic acid and phenanthrene solutions. The weights of benzoic acid and phenanthrene were the same for each of the three temperatures corresponding to a given experiment number.

Theory.—Since the vapor pressures of the two solutions must be equal at equilibrium, the mole fraction of solvent should be the same for each solution (in accordance with Raoult's law).

$$\frac{C_1/M_1}{C_1/M_1 + C_2/M_2} = \frac{C_1'/M_1}{C'/M_1 + C'/M_2'} \qquad (2)$$

In equation (2) C_1 equals the weight per cent. of benzene in the solution of phenanthrene and C_2 equals the weight per cent. of phenanthrene. Likewise C_1' and C_2' refer to the weight per cent. of benzene and benzoic acid in the benzoic acid solution. Finally, M_1 and M_2 equal the molecular weights of benzene and phenanthrene (respectively) and M_2' equals the apparent molecular weight of the benzoic acid.

Solving for M_2' from equation (2) gives

$$M_2' = (C_1C_2'/C_1'C_2)M_2 \qquad (3)$$

If M_0 equals the molecular weight of the dimer of benzoic acid, then α, the degree of dissociation of the dimer, will be given by

$$\alpha = (M_0/M_2') - 1 \qquad (4)$$

In accordance with the law of mass action the equilibrium constant for reaction (1) is given by the equation

$$K = 4\alpha^2C/(1 - \alpha) \qquad (5)$$

where C is the formal concentration of dimer in moles per liter of solution.

If ΔH for the dissociation is assumed constant, integration of van't Hoff's equation gives

$$\log_{10} K = -(\Delta H/2.303RT) + \text{const} \qquad (6)$$

Plotting $\log_{10} K$ against the reciprocal of the absolute temperature yields the heat of dissociation.

Calculations.—To determine the weight percentages of phenanthrene or benzoic acid in the solutions it is necessary to have some density data. For this purpose the following density equations were derived from data given in the "International Critical Tables"[6]

Benzoic acid in benzene

$$d^t_4 = 0.87360 - 0.001081(t - 25) + 0.001705C + 0.00000395C\ (t - 25) \qquad (7)$$

Phenanthrene in benzene

$$d^t_4 = 0.87360 - 0.001081(t - 25) + 0.001876C + 0.000005707C\ (t - 25) \qquad (8)$$

In these equations C equals the weight per cent. of solute and t the temperature in degrees centigrade. Equations (7) and (8) combined with the data of Table I enable one to calculate values for the weight percentage of the substances in the solutions.

By means of equations (3), (4) and (5) equilibrium constants for reaction (1) were then calculated. The numerical results are summarized in Table I. Since α is generally small compared to unity, it is seen that a small error in the apparent molecular weight M_2' gives rise to a large error in K. For example if M_2' were in error by 0.1% when $\alpha = 0.1$, then K would be in error by over 2.3%, or over 23 times as much as M_2' on a percentage basis. Thus the agreement among the different values of K is not as good as might be desired, although the accuracy of the experiments as judged from the values of M_2' would be quite satisfactory.

By methods of least squares the best equation of form (6) which can be fitted to the data is found to be

$$\log_{10} K = 3.790 - (1977/T) \qquad (9)$$

The probable error in $\log_{10} K$ computed from equation (9) is 0.6%, while the probable error of a single measurement of $\log_{10} K$ is about 1.6%. Although the uncertainty in $\log_{10} K$ is not bad, the uncertainty in K itself is considerably greater. Working backward it can be shown that the probable error in M_2' is less than 0.2%. The largest source of error is no doubt connected with the equilibrium volume readings. Deviations from Raoult's law for reasons other than association as well as temperature gradients in the apparatus might also contribute.

From equation (9) the heat of dissociation for the dimer is $\Delta H = 9000 \pm 400$ cal. This is in agreement with Hendrixson's[4] value of 8710 cal. obtained by study of the distribution of benzoic acid between benzene and water.

For one of the hydrogen bonds in the benzoic acid dimer may be assigned a strength one-half of that quoted above, namely, $\Delta H = 4500 \pm 200$ cal.

Summary

The association of benzoic acid in benzene is studied by an indirect vapor-pressure-lowering method assuming Raoult's law and using phenanthrene as a standard assumed to be unassociated. The dissociation constant for the dimer of benzoic acid is found to be expressed by the equation $\log_{10} K = 3.790 - 1977/T$ with a

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(6) "International Critical Tables," Vol. III, pp. 179 and 181

probable error in calculated $\log_{10} K$ of 0.6%. The heat of dissociation of the dimer of benzoic acid is computed to be 9000 ± 400 cal.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Reversible Photochemical Processes in Rigid Media. A Study of the Phosphorescent State

BY GILBERT N. LEWIS, DAVID LIPKIN AND THEODORE T. MAGEL

Introduction

When light is absorbed by an organic substance dissolved in a rigid solvent, various processes may occur. Radicals, ions or electrons may be thrown off, and in another paper we shall describe several interesting phenomena of this type. On the other hand, even without losing any of its parts, the molecule which is absorbing light may reach an excited state in which it persists, sometimes for a second or more, and then returns to the normal state with emission of light. This afterglow, or phosphorescence, is the subject of this paper. The phenomenon of phosphorescence has been studied extensively with the mineral phosphors, and with dyes adsorbed on various materials, in which latter class we may include the so-called solutions in substances like gelatin and collodion. In order to simplify the problem we shall limit our attention to phosphors consisting of organic dyes dissolved in a homogeneous non-crystalline solvent. Here also there is an extensive literature and we shall attempt in the remainder of this introduction to present briefly the information hitherto existing regarding such phosphors.

That dyes phosphoresce when dissolved in liquids which have been supercooled until they reach a rigid glassy state was discovered by Schmidt[1] as early as 1896. Tiede[2] found that powerful phosphors were obtained by dissolving dyes in fused boric acid, the phosphorescence depending on the way the boric acid is treated and the amount of water allowed to evaporate.

There has been some controversy as to the true law for the rate of phosphorescent decay, but the work of Schischlowski and Wawilow[3] and of Lewschin and Vinokurov[4] indicates that when the phosphorescence is due to a single excited substance the rate of decay is exponential. In other words, it is a reaction of the first order. If the process were due to the ejection of some part of the molecule, which then returned slowly, owing to the high viscosity of the medium, the order of the reaction would depend upon the distance of ejection but would never be of the first order.

Phosphorescence is not merely an extension of the life of ordinary fluorescence.[5] Indeed, most dyes show two phosphorescent bands, representing two processes so different that Perrin[6] proposed the use of the two names, "true phosphorescence" and "fluorescence of long duration." However, we prefer to keep the name phosphorescence for the total afterglow and avoid implications by speaking of the alpha and the beta process, respectively.

The alpha process gives a band that is indistinguishable from the fluorescence band, while the beta band is of lower frequency. The velocity of the alpha process increases rapidly with temperature, while that of the beta process is far less dependent upon temperature. Consequently at low temperatures the beta band alone is usually observed. Another difference is found when the phosphor is excited by polarized light, in which case the alpha emission shows a large degree of polarization while the beta band shows little or no polarization. Jablonski[7] has interpreted some of these facts by assuming that a single excited state is responsible for both of these processes and that while the beta process is essentially spontaneous, the alpha process requires thermal activation up to the fluorescent state. We shall find it possible to give a quantitative corroboration of this theory.

Spectroscopic Study of the Alpha and Beta Bands of Fluorescein in Boric Acid Glass

Fluorescein, as used in research upon luminescence, has not always been the same substance.

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(1) Schmidt, *Ann. Physik*, **58**, 103 (1896).

(2) Tiede, *Ber.*, **53**, 2214 (1920); Tiede and Wulff, *ibid.*, **55**, 588 (1922).

(3) Schischlowski and Wawilow, *Physik. Z. Sowjetunion*, **5**, 379 (1934)

(4) Lewschin and Vinokurov, *ibid.*, **10**, 10 (1936).

(5) Wawilow and Lewschin, *Z. Physik*, **35**, 920 (1926).

(6) R. Delorme and F. Perrin, *J. phys. radium*, **10**, 177 (1929).

(7) Jablonski, *Z. Physik*, **94**, 38 (1935).