is the same as assumed above, the resulting parameters are those given below along with the results of the electron diffraction study.[3]

	This research	Electron diffraction[3]
<FCF	109° 15′ ± 25′	110°
C–F	1.321 ± 0.005 Å.	1.321
C–C	1.311 ± 0.005 Å.	1.311 ± 0.035 Å.
<HCH	120° (assumed)	117° ± 7°
C–H	1.10 ± 0.05 Å.	1.07 ± 0.02 Å.

The CH distance corresponding to our choice of the HCH angle is 1.10 Å. A change in the angle of 9° changes the CH distance by 0.05 Å., but only changes the other parameters by less than 0.005 Å. Thus the microwave data still leave the geometry of the CH_2 group somewhat uncertain, but defines the remaining parameters quite precisely, since the actual HCH angle can hardly be expected to differ so greatly from 120°.

The measured FCF angle is nearer to the tetrahedral value than to that of 120° expected on the usual assumption that the σ-bonds are formed with sp^2 hybrids. It is interesting to note that near-tetrahedral values of the corresponding angle are not unusual in the substituted ethylenes, though the angle reported for ethylene itself[8] is 119° 55′. The particularly small value of the FCF angle is also in line with that reported[1] for CH_2F_2.

Comparison of the C–C distance with that found for ethylene[8] indicates that there is appreciable triple-bond character in the bond, an effect that may be associated with the closing of the FCF angle.

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[CONTRIBUTION FROM SOUTHERN METHODIST UNIVERSITY]

Experimental Investigation of the Distribution of Salicylic Acid between Cyclohexane and Water

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The distribution of salicylic acid between water and cyclohexane was investigated at various temperatures from 24.00 to 55.00° and at concentrations from 10^{-4} to 10^{-2} mole per liter in water and cyclohexane. The concentrations were determined spectrophotometrically. In the more dilute concentrations, the dimerization of salicylic acid in cyclohexane was found to be negligible; and from the data in this region the ionization and distribution constants were obtained. In the more concentrated regions the dimerization became appreciable; and from the data in this region the dimerization constant was calculated. With these constants known as a function of temperature, the heats, entropies and free energies of dimerization, distribution and ionization were calculated.

In spite of the numerous references to salicylic acid in the literature there are very few data on the dimerization of salicylic acid in non-polar solvents. By studying the distribution of salicylic acid between cyclohexane and water not only can the distribution coefficient be obtained, but also the ionization constant of the salicylic acid in water and the dimerization constant in cyclohexane. Furthermore if determinations are made at different temperatures the various enthalpy, free energy and entropy changes can be calculated.

Experimental

Materials.—Matheson practical grade cyclohexane was used. The cyclohexane was purified by passage through a column of activated silica gel in accordance with the procedure of Graff, O'Conner and Skau.[1] Salicylic acid was recrystallized from cyclohexane and then sublimed.

Spectrophotometric Measurements.—The concentrations of salicylic acid in both the cyclohexane and water layers were determined spectrophotometrically using a Beckman DU spectrophotometer. For each solvent, solutions of known concentration were prepared ranging from 10^{-4} to 10^{-2} mole per liter. The standard solutions in each solvent were saturated with respect to each other. Salicylic acid has absorption maxima in water at 231 and 296 mμ and in cyclohexane at 240 and 310 mμ. Beer's law was obeyed at all four peaks.

The following equations were found to relate A, the absorbance, to C_g, the concentration of salicylic acid in grams of acid per gram of solvent

Water	231 mμ	$C_g = 2.09 \times 10^{-5} A$
Cyclohexane	240 mμ	$C_g = 2.08 \times 10^{-5} A$
Water	296 mμ	$C_g = 3.96 \times 10^{-5} A$
Cyclohexane	310 mμ	$C_g = 4.32 \times 10^{-5} A$

All readings were taken in triplicate with an average variation of 0.002 absorbance units.

Distribution Method.—Preliminary measurements were made to determine the approximate relation between equilibrium concentrations of the aqueous and cyclohexane solutions of salicylic acid. With this information seven different mixtures were made up with concentrations varying from about 10^{-2} to 10^{-4} mole per liter. The mixtures were placed in glass-stoppered Pyrex bottles in a constant temperature bath and allowed to equilibrate for three days with occasional shaking. At the end of this time samples were withdrawn from each layer, diluted by weight if necessary to bring the concentration into the spectrophotometric range, and the absorbance determined.

This procedure was repeated daily until constant concentration values were obtained. Almost always equilibrium was obtained within a three-day period. Using the known dilution factor, the concentrations of salicylic acid in the water and cyclohexane layers were calculated. The concentrations were converted to moles per liter, assuming the solutions to be so dilute that the solvent and solution densities could be considered identical.

This procedure was repeated for all the solutions at seven different temperatures, 24.00, 29.50, 32.00, 36.00, 40.05, 47.13 and 55.00°. The temperature was controlled to within 0.01° by a Sargent Thermonitor unit.

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(1) M. M. Graff, R. T. O'Conner, and E. L. Skau, *Ind. Eng. Chem. Anal. Ed.*, **16**, 556 (1944).

Results

Representative data obtained for the 24.00° run are shown in Table I. Calculations of the various equilibrium constants from these data were considerably simplified when it was found that at the most dilute concentrations the dimerization of salicylic acid in cyclohexane was negligibly small.

TABLE I

DATA OBTAINED CORRELATING CONCENTRATION OF SALICYLIC ACID IN WATER AND IN CYCLOHEXANE FOR TEMPERATURE OF 24.00°

Mixture	Molar concn. (moles/l.) C_w	C_c	C_w/C_c	$\sqrt{1/C_c}$
I	0.000650	0.0000261	35.3	183
II	.00135	.0000443	30.4	147
III	.00197	.0000758	26.0	115
IV	.00328	.000218	15.0	67.7
V	.00648	.000753	8.61	36.5
VI	.00777	.00106	7.33	30.7
VII	.00857	.00129	6.63	27.8
VIII	.0152	.00601	3.80	15.9

The three equilibria involved are, first the ionization of salicylic acid in water, second the dimerization of salicylic acid in cyclohexane, and last the distribution of the undimerized and undissociated salicylic acid between the water and the cyclohexane layers. If C_w is the spectrophotometric value obtained for the total concentration in moles per liter of the salicylic acid in water and a represents the moles per liter of the acid which have ionized, then the ionization constant, K_i, may be written as

$$K_i = \frac{a^2}{C_w - a} \qquad (1)$$

In the cyclohexane layer, if C_c represents the total concentration of acid and b the concentration of single molecules which have associated in moles per liter then the dimerization constant, K_{dim}, is

$$K_{dim} = \frac{{}^1/_2\, b}{(C_c - b)^2} \qquad (2)$$

The distribution constant, K_d, which involves undissociated and undimerized salicylic acid then becomes

$$K_d = \frac{C_w - a}{C_c - b} \qquad (3)$$

When the concentration of acid in cyclohexane is so low that b may be assumed to be negligibly small compared to C_c then (3) becomes

$$K_d = \frac{C_w - a}{C_c} \qquad (4)$$

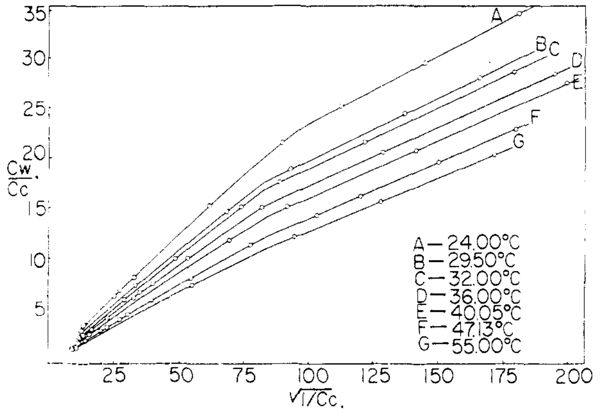

Fig. 1.—Graphical data from which ionization, distribution, dimerization constants can be calculated.

Under these conditions equations 1, 2 and 4 may be combined to give

$$\frac{C_w}{C_c} = K_d + \sqrt{\frac{K_i K_d}{C_c}}$$

Hence, if dimerization can be neglected in the regions of extreme dilution a plot of C_w/C_c *vs.* $\sqrt{1/C_c}$ should be linear with a slope of $\sqrt{K_i K_d}$ and an intercept of K_d.

In Fig. 1 the curves obtained at the various temperatures are shown. Values of K_d and K_i were calculated from the linear portion of each plot; and then with these values, from the data in the curved region, the K_{dim}' s were calculated. These are shown in Table II.

TABLE II

EQUILIBRIUM CONSTANTS INVOLVED IN THE DISTRIBUTION OF SALICYLIC ACID BETWEEN CYCLOHEXANE AND WATER

Temp., °C.	Ionization constant $K_i \times 10^{-3}$	Distribution coefficient K_d	Dimerization constant K_{dim}
24.00	1.78	10.4	1393
29.50	2.32	7.25	619
32.00	2.68	6.42	446
36.00	3.18	5.05	243
40.05	3.91	3.98	143
47.13	5.18	2.80	61.0
55.00	6.88	1.83	23.7

The plots of log K *vs.* $1/T$ for each of the equilibrium constants gave good straight lines. The average deviation of the points from a straight line in each case was less than five parts per thousand. From the slopes of these lines, the corresponding values of $\Delta H°$ were calculated in accordance with the van't Hoff equation. These are listed in Table III. Values of $\Delta F°$ and $\Delta S°$ were also calculated and are included in Table III.

Discussion

Most of the previous determinations of the ionization constant of salicylic acid in water have been made at 25°.[2,3,4,5,6] All of the values noted by different investigators lie close to 1.0 × 10^{-3} at this temperature, while in this investigation 1.9 × 10^{-3} was observed. The reason for this difference is not known. It does not seem likely that the small amount of cyclohexane dissolved in the water would be enough to give rise to appreciable error. Also, since the value of K_i was obtained in the extremely dilute solution region, any discrepancy cannot be attributed to the deviation of the activity coefficients from unity. The heat of ionization is also much greater than that reported by Bradley and Lewis.[4] There are several excellent review articles concerned with the hydrogen bond and dimerization in which thermodynamic con-

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(3) H. O. Jenkins, *Nature*, **151**, 561 (1943).

(4) F. Bradley and W. C. M. Lewis, *J. Phys. Chem.*, **29**, 782 (1925).

(5) J. Shorter and F. J. Stubbs, *J. Chem. Soc.*, 1180 (1949).

(6) B. Jones and J. C. Speakman, *ibid.*, 19 (1944).

TABLE III

THERMODYNAMIC VALUES OBTAINED IN SALICYLIC ACID–CYCLOHEXANE–WATER SYSTEM

Heat of ionization, 8150 cal./mole; heat of distribution, −10500 cal./mole; heat of dimerization, −24500 cal./mole.

	Free energy change (cal./mole)			Entropy Change (cal./mole degree)		
Temp., °C.	Ionization	Distribution	Dimerization	Ionization	Distribution	Dimerization
24.00	3738	−1383	−4268	14.9	−30.7	−68.1
29.50	3652	−1190	−4170	14.9	−30.7	−67.2
32.00	3595	−1128	−3705	14.9	−30.7	−68.1
36.00	3528	−996	−3370	15.0	−30.7	−68.3
40.05	3452	−859	−3082	15.0	−30.7	−68.4
47.13	3330	−655	−2611	15.1	−30.7	−68.3
55.00	3250	−395	−2068	14.9	−30.8	−68.4

stants are calculated and experimental methods discussed.[7–9] One objection to the distribution method is the possibility that the small amount of water present in the organic layer will form a hydrate with the acid being studied, increasing the solubility of the acid appreciably over that in the anhydrous organic solvent (see Lassettre[7]). Consequently, the solubility of salicylic acid in both anhydrous and water-saturated cyclohexane was investigated, but no significant difference found. Another objection is that the solvent in which the dimerization is taking place will influence the dimerization to some extent, and therefore the values obtained from solution studies will not necessarily agree with those from vapor studies. Indeed, the fact that the acid dissolves in the solvent indicates that some interaction between the two must take place and that the acid molecules will be partially solvated. Moelwyn-Hughes, Davies and their colleagues[10,11] have found that the magnitude of this effect is a function of the dielectric constant of the solvent, with the values of the heat and entropy of dimerization obtained by distribution methods approaching the vapor method values as the dielectric constant of the solvent decreases. In this respect cyclohexane should give better values than benzene or carbon tetrachloride.

Allen and Caldin have compiled values for the entropy and enthalpy changes involved in the dimerization of many different acids. For aliphatic acids, vapor phase measurements give values of ΔS° of about −36 e.u., and for ΔH° about −14 kcal./mole. They found that the value of ΔS° was in good agreement with the value based on the change in translational and rotational degrees of freedom in dimerization. In solution, as expected, the values are higher, ΔH° being about −8 kcal./mole and ΔS° ranging from −15 to −22 e.u. with concentrations expressed in moles/l. units or −21 to −28 in atmospheres. This variation in the entropy change then gives a measure of the increase in order of the monomers due to partial solvation.

Relatively little work has been done on aromatic acid. Many years ago Hendrixson[12] measured the ΔH° for both benzoic acid and salicylic acid by the investigation of the distribution of these acids between water and benzene, and water and chloroform. The values of ΔH° obtained for benzoic acid were −8.35 kcal./mole for the chloroform and −8.71 kcal./mole for the benzene systems. These values are in good agreement with those determined later by other investigators using different methods.[13,14]

The values of ΔH° for salicylic acid obtained by Hendrixson were −5.63 kcal./mole for benzene and −7.68 kcal./mole for chloroform.

The values obtained for ΔS° and ΔH° in this investigation of salicylic acid not only are considerably different from those obtained by Hendrixson, but they are also much different from the general values obtained for other acids. In the general reaction 2 monomer → dimer, the total entropy change can be considered to be made up of two parts.[15] The first is the change due to the translational and rotational degrees of freedom, and the second is the change due to the vibrational degrees. The first term must be negative since three translational and three rotational degrees of freedom are lost on association. The vibrational contribution, on the other hand, is positive since new vibrational degrees result from the association process. The value of the total entropy change on association for salicylic acid is about equal to the translational and vibrational contribution expected. The vibrational term, then, must be quite small indicating that the dimer bonds are very strong. This is consistent with the high value of the heat of dimerization observed.

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