

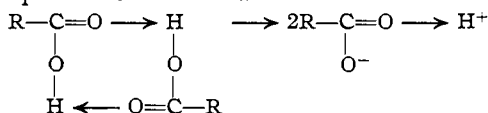
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

## The Electron-Sharing Ability of Organic Radicals. XII. The Effect of the Radicals on the Degree of Association of Polar Molecules

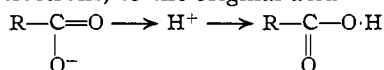
BY FRANC A. LANDEE AND I. B. JOHNS

The association of carboxylic acids has been assumed to be due to the formation of hydrogen bridges between carboxyl groups, as first suggested by Latimer and Rodebush.<sup>1</sup> This structure is known to be correct in the case of the formic acid complex from the investigation of the electron diffraction of formic acid vapor by Pauling and Brockway.<sup>2</sup>

Just as a solvated acid ionizes to give a solvated proton and an acid anion, the dimer might be expected to "ionize" as follows



The resulting ion would rearrange, by a simple shift of electrons, to the original acid



Obviously, the stronger the acid the greater the tendency toward scission of the original O—H bond and hence the greater will be the tendency toward dissociation of the dimer. Thus for strong acids the degree of association should be relatively less than for weak acids.

The effect of substituent radicals on the degree of ionization of the carboxyl group has been the subject of several papers in this series.<sup>3</sup> It has been shown to be general that the properties of any polar group are functions of the electron-sharing ability of the radical to which it is linked. The work presented in the present paper shows that the degree of association of the carboxylic acids is likewise dependent on the electron-sharing ability of the radicals attached to the polar group. In the following paper the effect of the substituent radicals in the solvent on the association of a solute is discussed.

### Experimental Part

#### A. Measurement of Association in the Vapor State

**Apparatus.**—The apparatus for making these determinations is represented in Fig. 1. The compound to be investi-

(1) W. M. Latimer and W. H. Rodebush, *THIS JOURNAL*, **42**, 1419 (1920).

(2) L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(3) R. M. Hixon and I. B. Johns, *THIS JOURNAL*, **49**, 1786 (1927); L. D. Goodhue and R. M. Hixon, *ibid.*, **56**, 1329 (1934); **57**, 1688 (1935).

gated was weighed in a sealed ampule. The fragile tip of the ampule was then bound tightly with small nichrome wire, and the entire assembly placed at the bottom of the barometric leg of the apparatus, as shown in Detail A of Fig. 1.

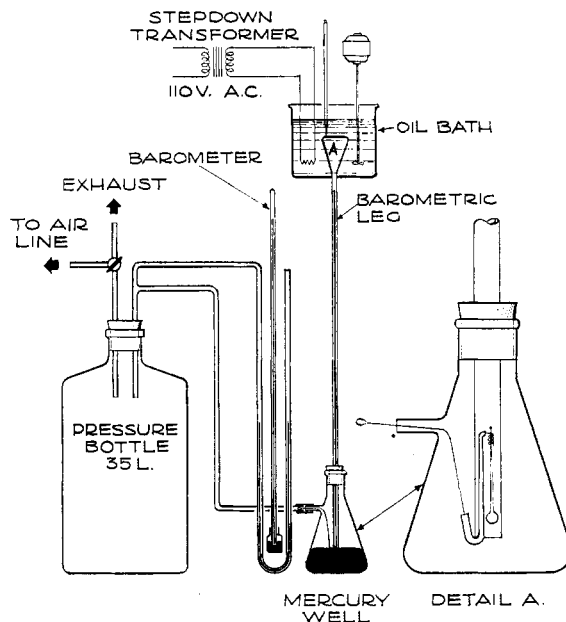


Fig. 1.

The oil-bath was then heated to about 160–170°, and the air pumped from the standard volume flask and barometric leg by means of a pump attached to the outlet tube of the mercury well. When suction is interrupted, the atmospheric pressure forces the mercury back up the barometric leg almost to the measuring index of the standard volume flask, A. By connecting the pressure bottle to the mercury well and applying a small amount of excess pressure, the mercury level could be brought to the calibration mark, indicating that the entrapped gases (Hg vapor, residual air, etc.) were occupying a volume of 142.22 cc. at the temperature of the oil-bath. The excess pressure necessary to do this was measured on the open-tube manometer to an accuracy of 0.2 mm. At the same time, the barometric pressure was read, and from these data the pressure of the residual gases was calculated. The pressure of the residual gases was measured over the entire temperature range to be used later in the measurement of the association.

After the preliminary standardization was completed, the mercury well was momentarily disconnected from the pressure bottle and the tip of the ampule was broken by a sharp pull on the wire. Immediately sufficient pressure was applied to drive the mercury and sample bulb well above the measuring index, thus avoiding trapping any of

TABLE I  
PHYSICAL PROPERTIES OF ACIDS OF THE TYPE RCOOH

Substance	Purity, %	B. p. (760 mm.) °C.	Dissociation const. in H <sub>2</sub> O, 25° C. × 10 <sup>4</sup>	E. S. A. of R.
<i>n</i> -Butyric acid	99.40	162	1.5	-1.45
Acetic acid	99.95	113	1.8	-1.40
Benzoic acid	99.99	249	6.6	4.2
Monochloroacetic acid	99.87	186	155	6.7
Dichloroacetic acid	100.80	191	5140	7.7
Trichloroacetic acid	99.92	196	121000	8.4

TABLE II  
MOLECULAR WEIGHT OF ACETIC ACID VAPOR AS A FUNCTION OF TEMPERATURE  
Sample weight 0.4960 g. Volume of flask 142.22 cc.

Temp., °C.	Total press., mm.	Residual gas press., mm.	Pressure of acid, mm.	Calcd. mol. wt.	Assoc. index, <i>A</i>	<i>K<sub>p</sub></i>
155	243.2	97.9	145.3	64.17	1.069	0.418
145	233.6	95.3	138.3	65.90	1.098	.662
135	222.6	92.6	130.0	68.55	1.143	1.14
125	210.9	90.1	120.8	71.90	1.198	1.94
115	199.1	87.8	111.3	76.05	1.267	3.38
105	187.3	85.2	102.1	80.75	1.346	6.02
95	174.7	82.4	92.3	86.95	1.449	12.2

the sample along the barometric leg. This level was maintained until all of the sample had volatilized, after which the pressures exerted by the sample at various temperatures were measured.

**Compounds Used.**—The choice of materials for this part of the investigation was simple, since only the carboxylic acids are known to be associated in the vapor state. As the effect to be studied was expected to be rather small, a series of acids of the type RCOOH was so chosen that the R groups concerned showed large variations in electron-sharing ability. Pertinent physical data on these compounds are presented in Table I. The purities were determined by titration of a weighed sample with barium hydroxide, using phenolphthalein as indicator. The numerical values of the electron-sharing abilities of the radicals were taken from the graph in the original paper by Hixon and Johns.<sup>3</sup>

The molecular weights of the acids in the gaseous phase were calculated from the pressure-volume relation. The association index, *A*, is defined as

$$A = \frac{\text{molecular weight found}}{\text{formula weight}}$$

The equilibrium constant for the association is expressed as

$$K_p = \frac{P_{(\text{RCOOH})_2}}{P_{(\text{RCOOH})}^2}$$

By using the association index, this can be rewritten

$$K_p = \frac{(A-1)}{(2-A)^2} \times \frac{760}{P_{\text{acid, mm.}}}$$

The data obtained for acetic acid are given in detail in Table II. The values of *K<sub>c</sub>* for acetic acid (calculated from *K<sub>p</sub>*) were plotted as a func-

tion of temperature and the heat of reaction at constant volume was calculated from the slope of the line. The value obtained, -15,700 cal., is in good agreement with the value reported by MacDougall<sup>4</sup> for this reaction, namely, -15,800 cal.

In Table III are given the data for trichloroacetic acid.

Neither *A* nor *K* was calculated from these data, since the acid is obviously not associated.

TABLE III  
MOLECULAR WEIGHT OF TRICHLOROACETIC ACID VAPOR AS A FUNCTION OF TEMPERATURE  
Formula weight 163.5; sample, 0.0408 g.

Temp., °C.	<i>P<sub>acid</sub></i>	Mol. wt. calcd.
165	48.7	162
160	47.9	163
155	47.6	162
150	47.5	160
145	46.4	162
140	45.6	163

The association index, *A*, is influenced both by temperature and pressure. Since in the gaseous state it is impossible to compare a series of acids at both the same temperature and the same pressure, it is most convenient to compare their association constants, *K<sub>p</sub>*, at various temperatures. These constants for all the acids studied are given in Table IV. Trichloroacetic acid is omitted from the table, since it showed no association at all.

TABLE IV  
ASSOCIATION CONSTANTS, *K<sub>p</sub>*, OF ACIDS OF THE TYPE RCOOH AS A FUNCTION OF TEMPERATURE

Temp., °C.	Butyric acid	Acetic acid	Monochloroacetic acid	Dichloroacetic acid
155	...	0.418	0.20	0.16
145	0.690	.662	.37	.34
135	1.05	1.14	.74	.56
125	1.90	1.94	..	..

#### B. Measurement of Association in Solution

**Apparatus.**—The apparatus used is shown in Fig. 2. The principle involved is the measurement of the pressures

(4) F. H. MacDougall, THIS JOURNAL, 58, 2585 (1936).

necessary to make the solvent and the solution boil at the same temperature.

The solvent or solution was contained in a three-necked flask. Boiling (always at a constant rate as indicated by the rate of dropping from the condenser tip) was at a temperature governed by the pressure above the liquid in the flask. This pressure was variable, and could be measured to 0.05 mm. by means of the inclined manometer shown in Fig. 2. As before, it was necessary to read the barometer at the beginning and end of each run, so that corrections might be made for any changes in atmospheric pressure during the course of a run. The actual boiling temperature was given by the tenth-degree thermometer, over the bulb of which the liquid was pumped by means of the vapor lift pump. With the apparatus shown, it was possible to boil either for six hours at a temperature constant to 0.01°, taking into account any changes in atmospheric pressure during this interval.

**Procedure.**—The actual method used in making a run was as follows. The round-bottomed flask was detached from the apparatus, cleaned and weighed to the nearest 0.1 g. About 250 cc. of solvent was added and weighed to 0.1 g. The flask was connected to the apparatus and the solvent boiled at atmospheric pressure and at the standard rate for about thirty minutes to expel all dissolved gases. The pressure was then gradually lowered until the solvent (ether) was boiling at a temperature of about 19.5°. After boiling for about ten minutes at this temperature to ensure temperature equilibrium, the pressure was gradually raised until a boiling point of approximately 19.95° was reached. From then on the slow leak of the apparatus was allowed to increase the pressure over the liquid, and hence raise its boiling point. Due to the large volume of the vacuum bottle, this change was very slow, and a period of from ten to fifteen minutes was always required for the boiling point to ascend to 20.00°. As soon as this temperature was reached, the inclined manometer and the barometer were read and the values recorded. Determinations were made in the same way for various temperatures up to the boiling point of the liquid at atmospheric pressure.

The solvent was then cooled well below room temperature, the condenser momentarily removed, and an accurately weighed quantity of the material to be investigated was added to the liquid. The condenser was then replaced, and the vapor pressure of the solution determined at various temperatures, exactly as before. At the end of a run the flask was reweighed to determine the loss of solvent, a loss usually amounting to about half a gram.

TABLE V

MOLECULAR WEIGHT OF NAPHTHALENE BY VAPOR PRESSURE METHOD

Calculated mole fraction of naphthalene, 0.0508; weight of ether, 215.5 g.; weight of naphthalene, 20.00 g.

Temp., °C.	Vapor press. of solvent, mm.	dP for solution, mm.	Mole fraction of solute	Mol. wt.
20.0	440.8	-22.41	0.0508	128.0
22.5	487.1	-24.65	.0506	128.7
25.0	537.0	-27.10	.0505	128.9
27.5	591.3	-29.99	.0506	128.7
32.5	713.3	-36.20	.0508	128.0

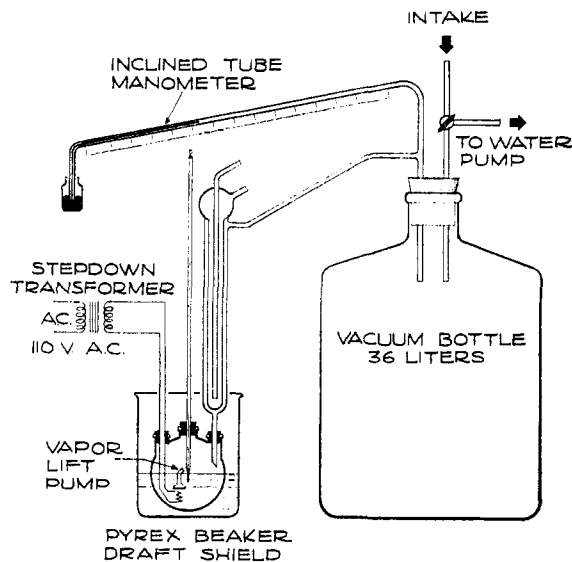


Fig. 2.

The method was checked using naphthalene as solute. This substance is known to exhibit a normal molecular weight in solution. The molecular weights were calculated using the simple Raoult formula

$$dP/P_0 = \text{Mole Fraction of Solute}$$

The data thus obtained are given in Table V, from which may be seen the excellent agreement obtained.

The method of measurement required the use of reasonably concentrated solutions. A solvent was therefore required in which the acids are associated only slightly. Diethyl ether is such a solvent, Beckmann<sup>5</sup> having found benzoic acid to show a molecular weight of 134.5 at 34° and at a concentration of 1.8 N. In Table VI are given the measured molecular weights of acetic acid in ether.

TABLE VI

MOLECULAR WEIGHT OF ACETIC ACID IN DIETHYL ETHER

Temp., °C.	Determn. . . . .	I	II	III
	Mole fr. . . . .	0.025	0.0492	0.0935
20.00		73.0	73.0	74.2
22.50		71.0	71.8	73.3
27.50		70.0	70.1	71.9
30.00		69.4	70.1	71.3
32.50		68.4	68.6	71.2

Since the reaction is not a simple one involving only double and single molecules, but instead involves solvated complexes, no attempt was made to calculate equilibrium constants. Instead, the association indices, *A*, representing the ratio of the measured molecular weight to the formula weight were calculated. In Table VII are presented these data at 0.05 mole fraction. Both

(5) E. Beckmann, *Z. physik. Chem.*, **3**, 603 (1889).

dichloro- and trichloroacetic acids showed molecular weights slightly less than the formula weight and accordingly were considered to be unassociated and were omitted from the table.

TABLE VII  
ASSOCIATION INDICES OF SOME CARBOXYLIC ACIDS IN ETHER

Temp., °C.	Acetic acid	Benzoic acid	Monochloroacetic acid
20.0	1.22	1.10	1.04
22.5	1.20	1.10	1.04
25.0	..	1.08	1.02
27.5	1.17	1.07	1.01
32.5	1.14	1.05	1.005

In addition to the results on diethyl ether, presented above, data were also obtained for the same series of acids using acetone and methyl acetate as solvents. In the latter slightly more association was found than was the case with ether solutions, but curves of the same general shape were obtained. In acetone, no association could be found for any of the acids.

### Discussion

In order better to show the relationship between the electron-sharing ability of radicals and the association of their compounds, these data have been put into graphical form. In Fig. 3 are plotted the association constants of the acids in the vapor state, as a function of the electron-sharing

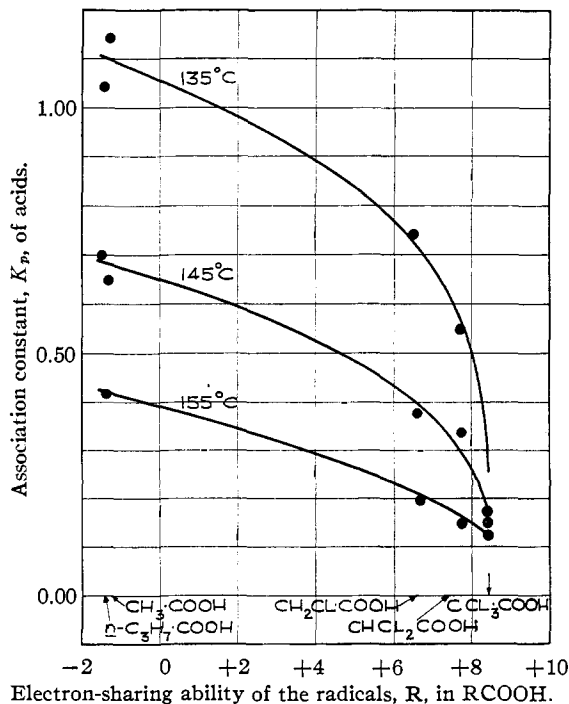


Fig. 3.

abilities of the radicals attached to the carboxyl group. In Fig. 4 are similarly plotted the association indices of these acids in solution. It is apparent from these curves that as the electron-sharing ability of the radical increases, the association of the corresponding acid decreases.

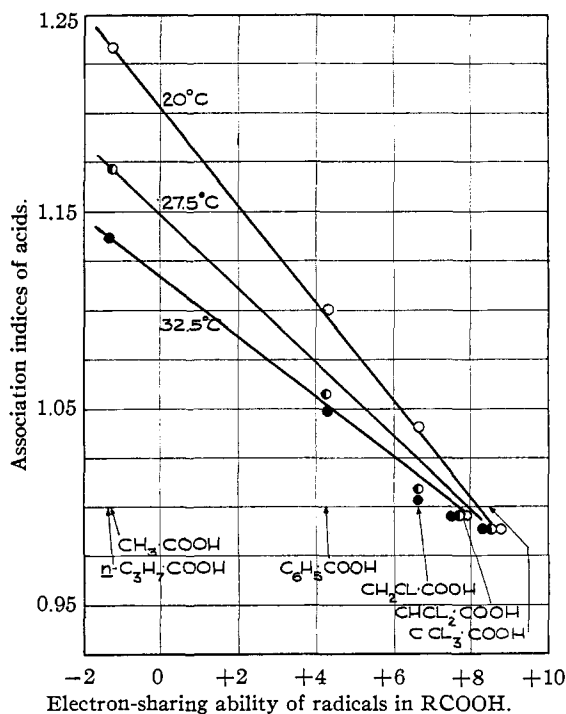


Fig. 4.

Auwers<sup>6</sup> and Biltz<sup>7</sup> and their co-workers made very extensive studies of the association of organic compounds in benzene and naphthalene. On plotting the per cent. association of compounds of the type ROH in benzene against the electron-sharing ability of the radicals, curves very similar to those shown in Figs. 3 and 4 are obtained. The same result is found for these compounds in naphthalene, although the association is definitely less than in benzene. The data were obtained by the cryoscopic method and the lesser degree of association in naphthalene can probably be ascribed to the higher temperature of fusion.

### Summary

Theoretical considerations have been made pointing out that the association (via hydrogen bridge formation) of organic compounds should be a function of the electron-sharing abilities of the radicals attached to the associating group.

(6) K. Auwers, *Z. physik. Chem.*, **18**, 595 (1895); **21**, 337, 342 (1896); **23**, 449 (1897); **30**, 300 (1899); **32**, 39 (1900); **42**, 512 (1903).  
(7) W. Biltz, *ibid.*, **29**, 249 (1899).

The association of a series of carboxylic acids, RCOOH, in the vapor state has been measured.

The association of the same series of acids has been measured in solution, using diethyl ether as solvent.

It is pointed out that the same theoretical considerations apply not only to the organic acids, but to any other types of organic compound which associate by hydrogen bridge formation.

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## The Electron-Sharing Ability of Organic Radicals. XIII. The Effect of the Radicals in the Solvent Molecule

By FRANC A. LANDEE AND I. B. JOHNS

As mentioned in the preceding paper, hydrogen bridge formation is of paramount importance in the association of compounds containing active hydrogen atoms, such as the carboxylic acids. The normalizing effect of many solvents is doubtless due to the formation of hydrogen bridges between the compound and the oxygen of the solvent. If this be true the electron donor power of the oxygen atom of a given solvent type, such as the ketones, nitro compounds, esters, etc., should be variable depending on the electron-sharing ability of the radicals attached to the carbonyl, nitro, carboxyl, etc., group.

In the formation of the covalent bond in the hydrogen bridge, there is no transfer of charge, or if such transfer takes place it must be completely and rapidly reversed. Accordingly such bonds should not be influenced by the dielectric constant of the medium.

The present paper shows that the normalizing effect of benzaldehyde on *p*-chlorophenol is due to the association of the solvent with the phenol, most probably by hydrogen bonding. It is also shown that the electron-sharing ability of the radicals in a series of ketones determines the normalizing power of these solvents on benzoic acid and on ethanol, and that the dielectric constants of these ketones have no noticeable influence.

### Experimental

**Proof that Association with the Solvent is the Cause of the Normalizing Effect.**—The method chosen to show the formation of complexes between the solvent and solute and the effect on the molecular weight of the solute was as follows. First, a substance of fair associating power was added to benzene and its molecular weight at various concentrations measured cryoscopically. Then to known solutions of this compound were added measured amounts of a non-associating compound and the total depression of

the freezing point measured. The apparatus used was that described in an earlier publication from this Laboratory.<sup>1</sup>

If there were no reaction between the two solutes then their effects would be additive. Any deviation from this behavior was interpreted as being due to association between the two solutes. Several pairs of compounds were investigated in this manner. Since all pairs gave the same results, data are presented only for *p*-chlorophenol and benzaldehyde.

The data pertaining to the molecular behavior of *p*-chlorophenol in benzene are listed in Table I.

TABLE I  
ASSOCIATION OF *p*-CHLOROPHENOL IN BENZENE AS A FUNCTION OF CONCENTRATION

Grams of solute in 100 g. of solvent	Moles solute in 100 g. solvent $\times 10^2$	F. p. depression, °C.	Calcd. mol. wt.	% Association
0.847	0.659	0.338	128.9	0
1.168	.91	.457	131	2
1.658	1.29	.640	133	3
2.010	1.56	.772	134	4
2.438	1.89	.921	136	6
3.155	2.45	1.172	139	8
3.210	2.49	1.172	141	10
3.912	3.04	1.391	144	12
4.341	3.38	1.535	145	13
4.609	3.58	1.599	148	15
4.964	3.86	1.562	151	17
5.29	4.12	1.794	152	18

Benzaldehyde in benzene exhibited a nearly normal molecular weight,  $109 \pm 1$ , over the range 1.4 to 7.1 moles/100 g. of solvent.

In Table II are presented the data for solutions of both benzaldehyde and *p*-chlorophenol in benzene.

The status of the two solutes can be determined from these data in the following way, using the second determination in Table II as example. Since there is present 0.0126 mole of benzaldehyde in one form or another, then  $0.648^\circ$  ( $0.0126 \times$

(1) I. B. Johns and R. M. Hixon, THIS JOURNAL, 56, 1333 (1934).