first paper[4] and attention should be called to the fact that this irregularity is less in the case of the ethanol measurement than in the case of the water measurement. The greatest deviations are to be found in the values reported by Goldschmidt for the acids in ethanol solution. It should be noted that this irregularity for the ethanol solutions does not hold for his measurements of the amines in the same solvent, all of the amine values being in substantial agreement with the calculated values. With the exception of formic acid, these deviations would appear to be associated with the less soluble compounds and are probably due to the deviations characteristic of saturated solutions. This point can be checked only as additional data are made available.

The ionization constants in methanol of the α-substituted pyrrolidines have been plotted in Fig. 2 to show that they also have a similar relationship to the corresponding values in water.[13] Attention should also be called to the fact that the equilibrium constants for the reaction

$$R_2Hg + HgI_2 \rightleftharpoons RHgI$$
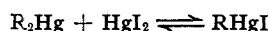
previously reported[16] were for ethanol solutions and that these values can be expressed as a

(16) Johns and Hixon, *J. Phys. Chem.*, **34**, 2226 (1930).

mathematical function of this same order of the organic radicals.

Summary

1. The ionization constants of acetic, *p*-toluic, benzoic, *p*-bromobenzoic and *m*-chlorobenzoic acids; of *n*-butylamine, *o*-chlorobenzylamine, *p*-toluidine, aniline, and *m*-chloroaniline; of the α-cyclohexyl-, α-benzyl-, α-(*p*-tolyl)-, and α-phenyl-pyrrolidines have been measured in methanol solutions using concentration cell methods analogous to the common procedure for water solutions.

2. The experimental difficulties in the measurement of the e. m. f. of alcoholic solutions due to the high internal resistance of the cells can be eliminated by the use of the vacuum tube potentiometer arrangement devised for measurements with the glass electrode in water solutions.

3. The ionization constants of the organic acids (R—COOH), of the primary amines (R—NH₂), and of the α-substituted pyrrolidines $\left(R-\boxed{}_N \right)$ can be expressed as a mathematical function of the electron sharing ability of the variable organic radicals (R) in the three solvents water, methanol and ethanol.

Electron-Sharing Ability of Organic Radicals. VIII. The Condensation of Mercaptans with Chloral

BY I. B. JOHNS AND R. M. HIXON

Earlier papers of this series have shown the relationship between an empirically determined property of organic radicals, the electron-sharing ability, and the polar properties of a number of series of compounds. The reactions studied can be grouped in the following classes: (A) ionizations in ionizing solvents—(1) in water, the ionization of the carboxylic acids,[1] the primary amines,[1] the organomercury nitrates,[2] the α-substituted pyrrolidines,[3,4] the α-substituted pyrrolines,[4] and the N-substituted pyrrolidines;[3] (2) in methanol, the ionization of the carboxylic acids,[5] the primary amines,[5] and the substituted

(1) Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927).
(2) Johns and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930).
(3) Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931).
(4) Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).
(5) See accompanying paper.

pyrrolidines;[5] (3) in ethanol, the ionization of the carboxylic acids,[5] and the primary amines.[5] (B) Metathesis in ethanol: (1) The reversible change of the organomercury iodides into mercuric iodide and di-organo mercury.[6]

These investigations have proved beyond doubt the hypothesis made in the first paper, that "The polar properties of any series of compounds such as ROH, RCOOH, ..., RNH₂, ..., etc., must be a function of the electron-sharing ability of R if we exclude from consideration under R all groupings which themselves have polar linkages."

The organic chemist is often more interested in nonionic reactions which may or may not be reversible. As yet, the only recognized measure of chemical affinity in a reaction is the diminution

(6) Johns and Hixon, *J. Phys. Chem.*, **34**, 2226 (1930).

of free energy.[7] Until this generalization is extended only reversible reactions can be safely used in comparing the affinities of organic radicals.

The condensation of various mercaptans with chloral to give the hemimercaptals, Eq. I, has been studied as an example meeting the above requirements.

$$Cl_3C—CHO + RSH = Cl_3C—CH(OH)SR \quad (Eq. I)$$

The equilibrium constants for the reaction in benzene were calculated from measurements of the freezing point depressions of known amounts
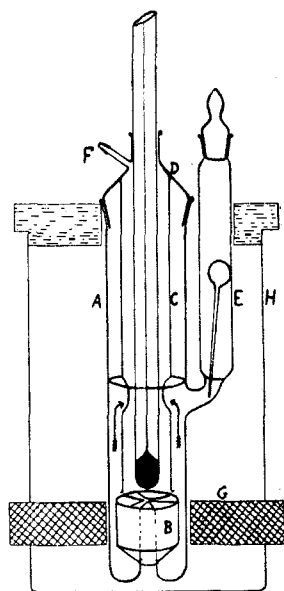

Fig. 1.—Freezing point apparatus.

of chloral and mercaptan, using a trace of hydrogen chloride as catalyst. The reaction could not be studied so accurately in the reverse direction since the hemimercaptals could not be obtained sufficiently pure. Some determinations were carried out, however, to show that the reaction is reversible.

The equilibrium constants for this non-ionic reaction in a non-ionizing solvent can be expressed as an exponential function of the electron-sharing abilities of the organic radicals, as was the case for the ionic reactions in ionizing solvents.

Materials

Chloral was prepared from the hydrate by shaking with cold concentrated sulfuric acid and distilling. The distillate was fractionated and the fraction boiling at 97° (747 mm.) was sealed in a large number of weighed ampoules of 0.2 to 1 g. capacity.

Ethyl, butyl and benzyl mercaptans (boiling points 35.5, 97 and 193–194°) were prepared by the method described by Ellis and Reid.[8] Thiocresol and thiophenol (boiling points 189.5 and 168°) and p-chlorothiophenol (m. p. 53°) were prepared by the reduction of the sulfonic acid chloride with zinc and sulfuric acid.[9] The mercaptans were also sealed in a large number of weighed ampoules.

Benzene was prepared by distilling a thiophene-free

(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 584.

(8) Ellis and Reid, THIS JOURNAL, **54**, 1674 (1932).

(9) "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 71.

product from phosphorus pentoxide and sealing it in ampoules of about 80 to 90 g. capacity.

Apparatus

The freezing point apparatus is shown in Fig. 1. It consists of an outer Pyrex container, A, in the bottom of which is sealed a pointed glass tube on which the rotor, B, turns. The cap, D, is ground into the outer tube and carries the Beckmann thermometer and the glass skirt, C. In the skirt above the bulb of the thermometer are two 15-mm. holes through which the liquid flows as indicated by the arrows, when the rotor is turning. The glass-stoppered side tube is used for filling and the tube F for drying the apparatus by suction.

The rotor, B, and the field, G, constitute a miniature induction motor. The rotor consists of a cylindrical shell of steel across the top of which are three spokes shaped to serve as a propeller. Across the bottom is a flat strip pierced by a hole through which the glass support passes. The whole rotor was first heavily copper plated to give it a highly conducting surface, and then gold plated to render it inert to the hydrogen chloride used as catalyst for the reactions. The weight of the rotor (15 g.) did not change more than one milligram throughout the whole series of determinations.

The field is laminated and has eight poles, each carrying three hundred turns. Alternate coils are connected in series to form two four-coil circuits. One of these is fed directly with the alternating current while the other is fed by a small transformer.

The whole apparatus was set in a water-tight tin container which was surrounded by cracked ice. The space between the glass parts and the walls of the container was filled with sufficient concentric cylinders of asbestos paper to permit the proper rate of cooling (0.05° per minute at the freezing point of benzene).

The principal advantages of this apparatus are: first, continuous, systematic and thorough stirring, the solid phase never becoming more concentrated at one place than at another, and, second, constant level of the liquid on the stem of the Beckmann. This latter point is extremely important for the stem correction of a Beckmann is very great and can be neglected when differences in temperature are measured only if the depth of immersion remains constant. Splashing the liquid on the stem of the thermometer will cause variations as great as 0.01° in the reading.

Method for Determination of Freezing Point Depressions.—After thoroughly drying the apparatus, about 80 g. of benzene was added from a weighed ampoule and its freezing point determined. Then a small amount (5 cc.) of dry hydrogen chloride gas was introduced into the side tube, E, and was washed into the benzene by repeatedly tipping the whole apparatus. The freezing point depression caused by the hydrogen chloride was determined. An ampoule of chloral was then opened and dropped stem down into E. After inserting the stopper, the side tube was warmed gently to drive out the contents of the ampoule. On cooling, benzene was drawn up and on warming was expelled again. By repeating the warming and cooling the ampoule was thoroughly rinsed out. The freezing point of the solution was then carefully deter-

mined, allowing an undercooling of not more than $0.1°$ and a cooling rate of not more than $0.05°$ per minute. Freezing was started in the undercooled solution by applying a current in the field coils sufficient, momentarily, to cause a rattling of the rotor. After freezing had begun the temperature rose to the freezing point and remained constant for more than five minutes without the slightest noticeable variation. Since this temperature is used in the calculations it was carefully checked to $0.001°$.

An ampoule of mercaptan was selected containing an amount as nearly as possible equivalent to the chloral. Its contents were expelled into the apparatus in the same way. After thorough mixing the freezing point was determined. Due to the slowness with which some mercaptans react with chloral, the apparatus was allowed to stand until constancy of freezing point indicated that equilibrium had been reached. This sometimes required as long as five days. The final freezing point was checked at least twice, allowing the apparatus to come to room temperature between determinations. The data are given in Table I.

TABLE I

THE DISSOCIATION CONSTANTS OF A SERIES OF HEMIMERCAPTALS IN BENZENE

RSH, g.	CCl_3CHO, g.	C_6H_6, g.	ΔT_{HCl}	ΔT_{RSH} Calcd.[a]	Obs.	$K_{dissoc.}$
C_4H_9SH						
0.2355	0.3877	83.94	0.024	0.160	0.032	1.6×10^{-3}
.2124	.3649	85.88	.028	.141	.032	2.3×10^{-3}
C_2H_5SH				i		
0.2129	.5391	77.11	.025	.228	.041	2.4×10^{-3}
.2404	.4970	82.58	.026	.240	.068	2.3×10^{-3}
$C_6H_5CH_2$SH						
0.2488	.3032	79.46	.022	.129	.036	3.0×10^{-3}
.2002	.2284	78.54	.067	.105	.033	2.6×10^{-3}
p-$CH_3C_6H_4$SH						
0.2674	.3124	84.83	.052	.130	.073	1.8×10^{-2}
.2065	.2528	82.81	.098	.103	.054	1.3×10^{-2}
C_6H_5SH						
0.2597	.3325	87.99	.046	.137	.082	2.2×10^{-2}
.4968	.6863	83.79	.017	.276	.149	3.6×10^{-2}
.6018	.8533	86.70	.034	.322	.130	2.0×10^{-1}
p-ClC_6H_4SH						
0.2748	.2969	83.68	.016	.116	.082	4.2×10^{-2}
.2725	.3033	87.60	.032	.110	.077	4.0×10^{-2}

[a] The value used for the molal freezing point constant of benzene was $5.1°$, cf. Peterson and Rodebush, J. Phys. Chem., **32**, 709 (1928). The ΔT_{RSH} given in Column 5 is that calculated on the basis of no reaction between the mercaptan and chloral.

Discussion of Results

The equilibrium constants can be calculated from the freezing point data on the assumption that Equation I represents the true reaction and that no complicating side reactions take place. The constants calculated on this assumption are presented in Table I.

There are four possible complications that must be considered: the influence of hydrogen chloride

concentration, the possibility of polymerization, the possibility of the formation of the complete mercaptal as well as the hemimercaptal, and the possibility that the reaction might not be reversible. The data in Table I show clearly that a three-fold change in the concentration of the catalyst has no effect on the equilibrium constants. This indicates that the hydrogen chloride acts only as a catalyst. Polymerization of the compounds has been proved definitely not to occur by the following procedure. The hemimercaptal of thiophenol and chloral was sealed in an evacuated tube connected to a manometer for the determination of its vapor pressure. A capillary containing gaseous hydrogen chloride was broken in the apparatus after it had been sealed. The vapor pressure has remained at 7 mm. for more than four months. It would thus seem unlikely that any polymerization could occur in solution during the few days each determination was run.

The evidence is quite conclusive that only the hemimercaptal is formed. Should the complete mercaptal form, water would be one of the products. At the freezing point of benzene the solubility of water is only 0.024% by weight,[10] or 0.00133 mole per 100 g. of benzene. No turbidity was observed on cooling to $0°$ a solution containing 0.4026 g. of chloral and 0.3984 g. of ethyl mercaptan in 6.00 g. of benzene, together with a trace of hydrogen chloride. The absence of water indicates that not more than 0.15% of the material could have formed the complete mercaptal. As evidence that should the reaction go beyond the hemimercaptal state the water would be noticed, experiments were tried using thiophenol and acetaldehyde and using ethyl alcohol and chloral. In both cases water separated as a distinct turbidity though the concentrations were less than 5% of the above.

To prove the reversibility of the reaction, nearly equimolar quantities of thiophenol and chloral were condensed by adding a trace of hydrogen chloride. The product was recrystallized three times from benzene and after drying *in vacuo* was melted and sealed in ampoules where it again solidified (m. p. $53°$).

Anal. Calcd. for $C_8H_7OCl_3S$: S, 12.45. Calcd. for $C_{14}H_{11}Cl_3S_2$: S, 18.30. Found: S, 13.-28, 13.32.

This analysis indicates the compound to be 85.1

(10) Tarassenkow and Poloshinzewa, Ber., **65B**, 186 (1932).

mole per cent. hemimercaptal. It was not found possible to purify it further, recrystallization and drying seeming to cause an increase in the formation of mercaptal.

A solution of 1.1135 g. of this preparation in 79.09 g. of benzene plus a trace of dry hydrogen chloride gave a freezing point depression of 0.279° which had changed to 0.367° at the end of five
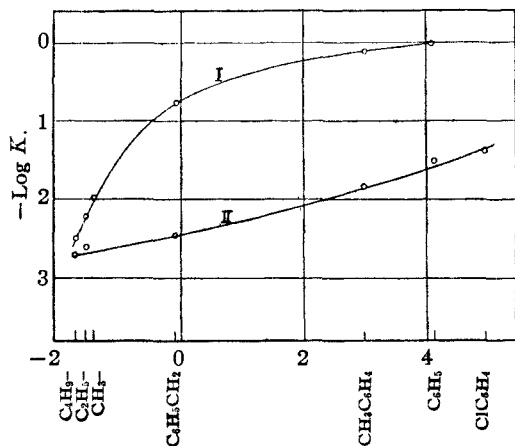
Electron-sharing ability of the radicals.

Fig. 2.—Curves showing the equilibrium constants as functions of the electron-sharing ability of the radicals, for the reactions: I, $2RHgI = R_2Hg + HgI_2$, and II, $Cl_3C—CHO + RSH = Cl_3C—CH(OH)SR$.

days and did not change further. Assuming the preparation to contain, as the analysis indicates, 14.9 mole per cent. complete mercaptal which could not dissociate in the absence of water and which should lower the freezing point 0.040°, the freezing point depressions were corrected, and the equilibrium constant found to be 1.6×10^{-2}. This is in good agreement with the values given in Table I and proves that the same equilibrium

point is reached from either direction. The accuracy is, however, much lower when using the previously prepared hemimercaptal due to lack of purity. For this reason all determinations in Table I were carried out using the separate components as the starting materials.

In Fig. 2 are plotted the equilibrium constants, $K_{dissoc.}$, from Table I together with those of the organo-mercuric iodides reported earlier.[6] The distribution of the radicals along the abscissa is the same as in the preceding papers. These curves can be represented by the equations

$$\log K_{RHgI} = -0.8e^{-0.7x}$$
$$\log K_{RSH} = 20(e^{0.09x-2.26} - 0.227)$$

The ionization constants of the acids and the amines were given by the equations[1]

$$\log K_a = 20(e^{0.5x - 6.6} - 0.24)$$
$$\log K_b = -20(e^{0.05x} - 0.75)$$

All of these constants are consequently interrelated by the electron-sharing ability, x, of the radicals. From the value of the constant, K, for any compound in any one of the series, the constants for the corresponding compounds (containing the same radical) in all the other series can be calculated.

Summary

1. A new type of freezing point apparatus is described.

2. The equilibrium constants for hemimercaptal formation are reported for ethyl, butyl, and benzyl mercaptans and for p-thiocresol, thiophenol, and p-chlorothiophenol with chloral.

3. The constants for these reactions are expressed as a mathematical function of the electron-sharing ability of the various radicals.