[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Equilibrium in Chloride Formation from Mono-, Di- and Triarylcarbinols

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A quantitative study of the equilibrium in the reaction

$$\mathrm{ROH + HCl = RCl + H_2O} \qquad (1)$$

has been undertaken for a series of compounds in which R is a mono-, di- or triarylmethyl radical. A list of the compounds selected for study appears in Table I. For these substances it has been found that equilibrium can be attained at 60° in a reasonable length of time, and that the reaction proceeds according to Eq. 1 without interference from the formation of other products.

The first experimental step follows a procedure used by Halford[2] in a study of the hydrolysis of triphenylchloromethane and triphenylbromomethane. A dilute benzene solution of the carbinol and chloride is brought to equilibrium with aqueous hydrochloric acid and the phases are separately analyzed. An equilibrium constant $K(1)$ is evaluated in accordance with Eq. 2, in

$$K(1) = \frac{C_{\mathrm{RCl}}p_{\mathrm{H_2O}}}{C_{\mathrm{ROH}}p_{\mathrm{HCl}}} \qquad (2)$$

which C represents concentration in benzene and p is the partial pressure taken from "International Critical Tables."[3]

In the present work, for the reactions involving the benzyl and p-xylyl alcohols and the diphenyl- and di-p-tolylcarbinols, the results have been extended to the vapor phase with the aid of partial pressures in benzene solution, to give vapor phase equilibrium constants which should not be in error by more than 15%. The corresponding extensions for the remaining diaryl compounds and for the non-volatile triaryl compounds are based upon estimates of the partial pressures and are therefore subject to a somewhat larger uncertainty.

Solutions of benzyl chloride, triphenylchloromethane and triphenylcarbinol in benzene are nearly perfect and permit the use of the relation $p = p^0N$ as a first approximation in obtaining the vapor phase constant. It is assumed that all of the chlorides and tri-p-tolylcarbinol will show similar behavior. On the other hand, the relation between partial pressure and mole fraction for the mono- and diarylcarbinols in benzene is more complicated, with the former showing the greater deviations from the perfect solution equation. We find that the partial pressure of the solvent is adequately expressed for the benzyl alcohol solutions by the equation $p_1 = p_1^0X_1$ where $X_1 = 1 - X_2 = AN_1/(AN_1 + N_2)$. It follows directly that $A = (N_2/N_1)\ (p_1/[p_1^0 - p_1])$, and in conformity with the Duhem–Margulis equation, that $p_2 = p_2^0\ X_2^{1/A}$. Since the solutions of p-xylyl alcohol and the diarylcarbinols in benzene are more nearly perfect than those of benzyl alcohol, it is safe to assume that the above relations may be used for all the carbinols.

The vapor phase constant may now be expressed as

$$K(\mathrm{g}) = \frac{p_{\mathrm{RCl}}p_{\mathrm{H_2O}}}{p_{\mathrm{ROH}}p_{\mathrm{HCl}}} = \frac{p^0_{\mathrm{RCl}}}{p^0_{\mathrm{ROH}}}\,\frac{N_{\mathrm{RCl}}}{X^{1/A}_{\mathrm{ROH}}}\,\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{HCl}}} = K(1)\,\frac{N_{\mathrm{ROH}}}{X^{1/A}_{\mathrm{RHO}}}\,\frac{p^0_{\mathrm{RCl}}}{p^0_{\mathrm{ROH}}} \qquad (3)$$

It follows from the definition of X that at low concentrations $X_{\mathrm{ROH}} = N_{\mathrm{ROH}}/A$. Consequently

$$K(\mathrm{g}) = K(1)\,\frac{p^0_{\mathrm{RCl}}}{p^0_{\mathrm{ROH}}}\,A^{1/A}N_{\mathrm{ROH}}^{(1-1/A)} \qquad (4)$$

In deriving Eq. 4 the concentration ratio of Eq. 2 has been replaced by the equivalent ratio of mole fractions. The factor by which the liquid phase constant must be multiplied in order to give $K(\mathrm{g})$ involves the vapor pressures of the pure liquid carbinol and chloride and the quantity A, which latter depends upon the partial pressure of benzene over solutions of the carbinols.

Although this treatment of the carbinol solutions provides a correction for association, its success cannot be explained in terms of a simple picture of the association equilibrium. If, for example, only a monomer and dimer were involved, and each acted as a perfect solute, the correction factor should increase with dilution. The observed situation suggests a stable dimer in equilibrium with a monomeric form of high fugacity.

Table I presents a summary of the liquid phase constants defined by Eq. 2. The vapor phase constants are included, for comparison, as the

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[1] From a dissertation submitted by Eugene B. Reid in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, 1939.

[2] J. O. Halford, THIS JOURNAL, 53, 105 (1931).

[3] "I. C. T.," Vol. III, p. 216.

TABLE I

EQUILIBRIUM IN THE REACTION $ROH(bz) + HCl(g) = RCl(bz) + H_2O(g)$ AT 60°

R	Time, days	C(moles/liter)		Wt.%	p, mm.			
		ROH	RCl	HCl	H_2O	HCl	K(l)	K(g)
Benzyl	57F	0.03240	0.05040	7.91	135.0	0.079	2672	1199
	57R	.02942	.05090	7.98	135.0	.081	2901	1238
p-Xylyl	68F	.01401	.04018	7.72	136.0	.074	5300	2229
	68R	.01240	.04530	8.03	135.0	.082	6015	2397
Diphenylmethyl	12F	.02237	.03316	13.32	118.4	.478	367	247
	11F	.02247	.03232	13.27	118.5	.470	363	245
	16F	.02125	.03283	13.33	118.4	.480	381	253
	15F	.01764	.04596	14.69	113.7	.755	393	247
	11R	.02109	.03602	13.68	117.0	.539	371	246
	12R	.01873	.03151	13.63	117.3	.530	373	238
	19R	.02760	.02182	11.75	124.3	.281	350	250
	19R	.03246	.02284	11.40	125.0	.254	346	259
	15R	.01494	.04518	15.08	112.3	.860	395	237
o-Methyldiphenylmethyl	16F	.01566	.02911	13.30	118.4	.475	463	316
	23F	.01592	.02670	13.36	118.2	.482	411	282
	14R	.01688	.03383	13.68	117.0	.539	435	303
	21R	.01721	.03350	13.71	117.0	.543	419	293
m-Methyldiphenylmethyl	14F	.01354	.03303	14.75	113.4	.771	359	209
	21F	.01282	.03724	14.77	113.3	.773	426	245
	14R	.01023	.03511	15.16	111.9	.884	435	234
	21R	.01060	.03474	15.17	111.9	.885	415	225
p-Methyldiphenylmethyl	26F	.01463	.04181	15.14	112.2	.880	365	217
	43F	.01455	.03852	15.07	112.4	.858	347	207
	23R	.01111	.03741	15.44	111.0	.975	384	211
	40R	.01188	.03664	15.33	111.5	.938	367	206
Di-*p*-tolylmethyl	29F	.02291	.03701	14.86	113.3	.800	229	178
	29R	.02068	.04034	15.22	111.8	.902	242	183
Di-*o*-tolylmethyl	29F	.01028	.04803	14.78	113.5	.778	688	..
	29R	.00914	.04670	15.12	112.2	.873	657	..
o-Chlorodiphenylmethyl	39F	.02396	.02816	14.81	113.7	.785	170	126
	39R	.02096	.03172	15.12	112.2	.873	195	139
p-Chlorodiphenylmethyl	35F	.01542	.03316	14.67	113.8	.749	327	198
	43F	.01288	.03106	14.89	113.2	.808	338	195
	35R	.01693	.03565	15.09	112.2	.863	274	170
	43R	.01614	.03420	15.18	111.9	.890	266	164
p,p'-Dichlorodiphenylmethyl	40F	.02095	.02254	14.94	113.0	.821	148	113
	40F	.01806	.01980	14.95	113.0	.822	151	111
	35R	.01299	.03216	15.06	112.5	.855	326	222
	40R	.01184	.03632	15.16	111.9	.884	388	258
p-Phenyldiphenylmethyl	19F	.00345	.01570	16.68	106.7	1.47	330	..
	38F	.01706	.03584	14.77	113.0	0.776	306	..
	17R	.00411	.02429	16.94	105.8	1.60	391	..
	32R	.01420	.04096	15.06	112.5	0.855	380	..
Triphenylmethyl	7F	.03742	.05850	21.65	86.8	7.68	17.7	28
	5F	.01552	.02528	21.97	85.5	8.55	16.3	26
	5R	.01879	.03386	22.25	84.4	9.33	15.8	25
	7R	.03360	.06220	22.25	84.4	9.34	15.8	25
Tri-*p*-tolylmethyl	6F	.01516	.03482	20.97	89.7	6.10	33.8	54
	6R	.01471	.03554	21.30	88.4	6.83	31.3	50

last column. In the second column the time of equilibration, in days, is followed by F or R, to indicate whether equilibrium was approached by the forward reaction or by the reverse reaction.

Materials.—Benzyl alcohol, benzyl chloride, diphenylcarbinol, triphenylcarbinol and triphenylchloromethane were obtained by purifying commercial samples, using vacuum distillation or recrystallization as required.

The authors are indebted to Professor W. E. Bachmann for the *p*-phenyldiphenylcarbinol and to Professor M. Gomberg for the tri-*p*-tolylchloromethane.

Tri-*p*-tolylcarbinol was obtained by hydrolyzing tri-*p*-tolylchloromethane and recrystallizing the initial product from petroleum ether.

p-Xylyl alcohol was prepared from *p*-tolualdehyde by the Cannizzaro reaction, recrystallized from petroleum ether and vacuum distilled.

Each of the isomeric methyldiphenylcarbinols and the di-*o*-tolylcarbinol were prepared by combining a Grignard reagent with a nitrile to give the imine hydrochloride, hydrolyzing and then reducing the resulting ketone with 2% sodium amalgam. *p,p'*-Dimethylbenzophenone was reduced to di-*p*-tolylcarbinol in the same manner.

In preparing the ortho and para chlorodiphenylcarbinols the ketones were obtained from nitriles by the Grignard reaction, then reduced by aluminum isopropylate. The reduction required eight hours. The corresponding reduction of *p,p'*-dichlorobenzophenone produced only a 75% yield of the carbinol in 24 hours.

Benzyl chloride was dried with potassium carbonate and calcium chloride and then subjected to repeated vacuum distillation. The final retention from middle fractions was 25%. The *p*-xylyl chloride used for vapor pressure measurements was purified in the same manner; the material used in the equilibrium measurements was prepared from *p*-xylyl alcohol by the action of 30% hydrochloric acid for one day at 60°, followed by extraction and vacuum distillation.

Thionyl chloride was used as described by Gilman and Kirby[4] to convert diphenylcarbinol to diphenylchloromethane. The crude product was distilled under reduced pressure.

The remaining chlorides were not isolated, but were used as benzene solutions obtained from the carbinols by the action of 30% hydrochloric acid. The benzene layer was recovered quantitatively, freed of hydrogen chloride and water and analyzed for the chloride before it was used in the equilibrium measurements. All of the substituted diphenylchloromethanes were handled in this manner. In addition the di-*p*-tolylchloromethane was isolated and purified for vapor pressure measurements.

Equilibrium Determinations.—The reaction vessels were 250-cc. tincture bottles with re-ground glass stoppers. A small amount of Cenco rubber base high melting stopcock grease was used to minimize leakage. In spite of these precautions leaks occasionally occurred, but losses were confined to the aqueous layer because of preferential wetting of glass by water, and the benzene solution was recovered quantitatively.

Carbinol or chloride was weighed to the amount of 0.005 to 0.01 mole into 100 cc. of benzene and subsequently mixed with 50 cc. of hydrochloric acid of appropriate strength. The reaction vessel was rotated in an air thermostat at 60.0 ± 0.2° for from about one week for the triaryl compounds to two months for the monoaryl compounds. After equilibration the benzene layer was separated, washed with ice water until the washings showed no chloride ion, then titrated with silver nitrate and sodium chloride as described below. The washing process ordinarily required fifteen minutes, but for the triphenyl compounds it was reduced to two minutes in order to prevent disturbance of the equilibrium. The tri-*p*-tolylchloromethane solution was titrated without washing and the necessary small blank correction for hydrogen chloride was determined separately.

A sample of the equilibrium aqueous layer was titrated for hydrochloric acid. Partial pressures of water and hydrogen chloride were taken directly from values tabulated for the reaction temperature, thus introducing an error due to the effect of dissolved benzene, which is soluble in water to about 0.5% at 60°. The water pressure should not be appreciably changed and that of hydrogen chloride should be only slightly increased. The error has been neglected.

Analytical Method.—To find the chloromethane content of a benzene solution, it was first diluted with isopropyl alcohol, excess of standard silver nitrate in isopropyl alcohol was added, and the excess was titrated with sodium chloride. About ten minutes was required for complete reaction of a diarylchloromethane with the silver nitrate, while benzyl or *p*-xylyl chloride required several hours of heating. The carbinol content at equilibrium was obtained by difference. The purified carbinols were analyzed as chloromethanes after conversion in benzene by the action of concd. hydrochloric acid for one or more days.

A potentiometric end-point was used. The apparatus included a silver wire indicator electrode, a normal calomel reference electrode, a 1 *N* potassium acetate–3% agar bridge, a simple potentiometer and a Leeds and Northrup type 2420A galvanometer. A fairly sensitive galvanometer was required because of the relatively high resistance of the non-aqueous solution.

Vapor pressures were measured with the Hickman, Hecker and Embree[5] apparatus, designed to determine a low equilibrium pressure over a boiling liquid. A water jacket constituted a satisfactory condenser for the substances which are liquids at room temperature. For the others a vapor jacket of chloroform or carbon tetrachloride insured condensation in the liquid state. The apparatus was satisfactory at pressures between 1 mm. and 10 mm. of mercury, provided that the temperature was not above 160°, where a pressure drift with the time became appreciable. Temperature was measured with a mercury thermometer graduated in tenth degrees and calibrated by comparison with Bureau of Standards calibrated thermometers numbered 46,126, 61,920 and 61,924. Because of difficulty with negative pressure readings, the butyl phthalate manometer described by Malmberg and Nicholas[6] was modified to provide for continuous evacuation of the reference side by a mercury diffusion pump.

The constants of linear equations based upon the vapor pressure data are shown in Table II.

TABLE II

VAPOR PRESSURES OF ARYLCARBINOLS AND ARYLCHLOROMETHANES

$\log p(\text{mm.}) = -A/T + B$

	A	*B*	Mean deviation %
Benzyl chloride	2601	8.804	0.9
Benzyl alcohol	3274	9.993	0.6
p-Xylyl chloride	2762	8.862	2.8
p-Xylyl alcohol	3352	9.908	2.0
Diphenylchloromethane	3680	9.631	2.5
Diphenylcarbinol	4045	10.236	2.5
Di-*p*-tolylchloromethane	3929	9.670	5.0
Di-*p*-tolylcarbinol	4267	10.264	3.3

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(4) Gilman and Kirby, THIS JOURNAL, **48**, 1733 (1926).

(5) Hickman, Hecker and Embree, *Ind. Eng. Chem., Anal. Ed.*, **9**, 264 (1937).

(6) Malmberg and Nicholas, *Rev. Sci. Instruments*, **3**, 440 (1923).

With each of the di-*p*-tolyl compounds, twenty measurements were made in a 30 degree temperature range. With the others, the number of measurements varied from fifteen to forty and the temperature range was 40 degrees. Readings were taken in about equal numbers for equilibrium approached from above and below saturation. The last column shows the average percentage deviation of the measured pressures from those calculated from the equations.

Table III is a list of the vapor pressures derived for the reaction temperature of 60° together with their ratios as required by Eq. 4. The values above 1.0 mm. lie within the practical measuring range and are therefore equivalent to direct measurements. Only a short extrapolation was required for the *p*-xylyl alcohol data. Direct extrapolation was used for the diphenylcarbinol and chloride, but for the less volatile di-*p*-tolyl compounds some further indication of the slopes of the lines was required. Use was therefore made of the Hildebrand[7] modification of Trouton's rule, which assigns the same entropy of vaporization to normal liquids at temperatures at which they have the same low equilibrium vapor concentration. According to this rule, the ratio of the desired slopes is equal to the ratio of the temperatures at which the quotient of the vapor pressure by the temperature is the same. The extrapolation for di-*p*-tolylchloromethane and di-*p*-tolylcarbinol could thus be based upon the more reliable data taken for diphenylchloromethane and diphenylcarbinol, respectively, without applying Hildebrand's generalization to any but very closely related compounds. The entropy of vaporization of carbinols which exhibit association is not the same as for normal liquids, but it is reasonable to assume that two very similar carbinols would have the same entropy of vaporization. To demonstrate this, a point was taken from the *p*-xylyl alcohol data, and, by using the benzyl alcohol curve, an extrapolation over a 40° range was performed. The result deviated from the measured value by about 2%. A similar trial with the corresponding chloro compounds over a 25° range produced a deviation of 1%.

Table III

Vapor Pressures of Arylcarbinols and Arylchloromethanes at 60°

R	p^0_{ROH}	p^0_{RCl}	$p^0_{\text{RCl}}/p^0_{\text{ROH}}$
Benzyl	1.46	9.90	6.72
p-Xylyl	0.700	3.72	5.34
Diphenylmethyl	0.0125	0.039	3.12
Di-*p*-tolylmethyl	0.0028	.0075	2.64

Total Pressure of Benzene Solutions.—In deriving Eq. 4 it was stated that solutions of the arylchloromethanes in benzene were nearly perfect and that the partial pressure of a carbinol over its benzene solution could be expressed in terms of a constant *A* which depends upon the benzene partial pressure. To demonstrate these points and to derive the constants for the carbinols requires only the measurement of the total pressures, since the solutes contribute very little to the pressure.

For the benzene–benzyl alcohol solutions an apparatus was used which permitted the mixing of known quantities of out-gassed solute from an evacuated buret with a weighed quantity of outgassed solvent in an evacuated flask. The entire composition range was covered in two runs by reversing the roles of solvent and solute. This apparatus was not satisfactory for benzyl chloride because of its tendency to dissolve stopcock grease. Benzyl chloride solutions of known composition were therefore placed in 100-cc. flasks and dissolved gases were removed by evacuation. The change in composition due to evaporation was estimated from the loss in weight. The blank

Table IV

Total Pressure of Benzene–Benzyl Alcohol Solutions at 25°

N (alc.)	*p*, (mm.)	*N* (alc.)	*p*, (mm.)
0.000	94.7	0.470	75.0
.081	91.5	.487	74.6
.125	89.9	.519	71.0
.215	87.4	.578	67.0
.294	84.0	.647	61.0
.350	81.6	.741	48.4
.399	79.4	.856	30.1
.433	77.5	.921	17.4
.443	77.0	1.000	0.1

Table V

Total Pressure of Benzene–Benzyl Chloride Solutions at 25°

N chloride	*p* (total), mm.	*p* (partial) mm., calcd.
0.000	94.7	94.7
.0643	88.6	88.5
.122	82.7	82.4
.279	70.2	68.8
.454	54.3	53.7
.643	37.4	36.6
1.000	1.25	0.0

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[7] Hildebrand, This Journal, **37**, 970 (1915).

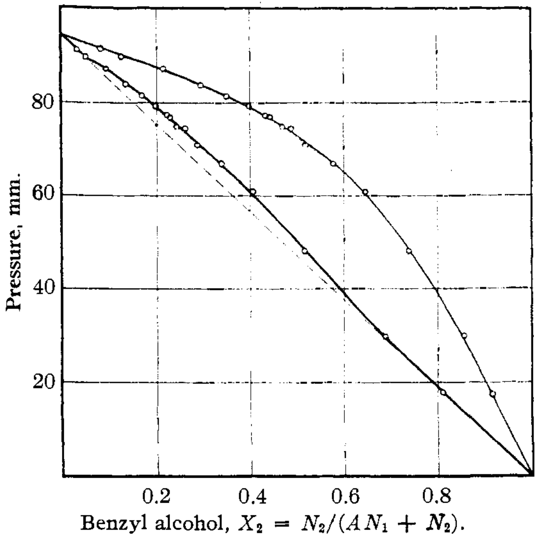

Fig. 1.—Benzene partial pressure, benzene–benzyl alcohol solutions at 25°: lower curve, $A = 2.68$; upper curve, $A = 1.00$ ($X_2 = N_2$).

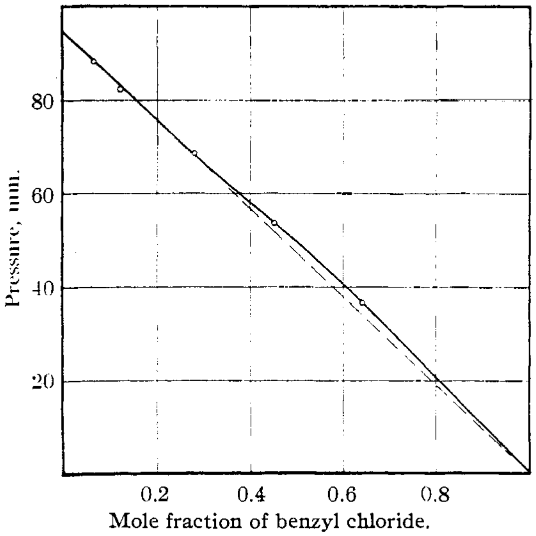

Fig. 2.—Benzene partial pressure, benzene–benzyl chloride solutions at 25°.

with benzene showed 0.5 mm. of air, for which a correction was applied to each measurement. Data for the benzene–benzyl alcohol system appear in Table IV and Fig. 1, and for the benzene–benzyl chloride system in Table V and Fig. 2. Pressures were measured with a mercury manometer and the temperature was held at 25° by means of a thermostat.

Both Fig. 2 and Fig. 1 show small positive deviations from the linear relation for the benzene partial pressure at concentrations of solute larger than those of the equilibrium measurements. This means that in dilute solutions the true solute partial pressures are a little larger than those used in deriving Eq. 4, but, since the error is small and tends to cancel between the carbinol and chloride, it has been neglected. To be strictly correct, the vapor pressure ratio of Eq. 4 should be replaced by a ratio of Henry's law constants. The correct ratio, derived by graphical integration from the benzyl alcohol and benzyl chloride data, at 25°, is 7% higher than the one used, but at higher temperatures and with the diaryl compounds, for which lower values of A have been found, the error should be much less.

For each of the remaining carbinol–benzene solutions, A values were derived from pressure measurements at one or two concentrations. The method of measurement was the same as that described for benzyl chloride, except that the solutions were more vigorously out-gassed, and each measurement was repeated after a second rapid evacuation. The data are collected in Table VI. The high values of A found at mole fractions above 0.2 for diphenylcarbinol and *p*-methyldiphenylcarbinol represent positive deviations from the linear relation similar to that appearing in the lower curve of Fig. 1.

TABLE VI

TOTAL PRESSURE OF CARBINOL–BENZENE SOLUTIONS AT 25°

R(OH)	N_2	p_1	A (25°)	A (60°)
Benzyl (A = 1.9 at 70°)	0.125	89.9	2.68	2.07
p-Xylyl	.151	87.8	2.23	1.75
Diphenylmethyl	.2116	82.8	1.86	
	.2063	82.2	1.69	
	.1532	85.6	1.63	1.40
p-Methyldiphenylmethyl	.2078	83.3	1.90	
	.1448	86.0	1.65	1.40
m-Methyldiphenylmethyl	.1644	84.7	1.64	1.40
o-Methyldiphenylmethyl	.1540	84.9	1.55	1.34
Di-*p*-tolylmethyl	.1550	84.4	1.49	1.30
o-Chlorodiphenylmethyl	.1648	84.2	1.57	1.35

The last column has been calculated to give A-1 at 60° a constant fraction of its value at 25°, with the fraction determined from benzyl alcohol for which the value at 60° has been obtained by linear interpolation from the measurements at 25 and 70°. It is observed that the meta and para methyldiphenylcarbinols have the same factor as diphenylcarbinol, and that likewise the factor is the same for the ortho chloro and ortho methyl derivatives. In calculating vapor phase equilibrium constants involving compounds not listed in Table VI, it is therefore assumed that A is the same for corresponding chloro- and methyldiphenylcarbinols. The value 1.0 has been used for the triarylcarbinols in accordance with the observation that triphenylcarbinol forms a nearly perfect solution with benzene.

When the pressure ratio of Table III is divided by the square of the corresponding A value from the last column of Table VI, the result is a constant for all four substances, 1.6 ± 0.1. If this behavior extends to include the non-volatile triaryl compounds, the pressure ratio should be 1.6 for both the phenyl and the *p*-tolyl derivatives. This ratio has been used, in the absence of any method of direct measurement, in calculating vapor phase equilibrium constants for chloride formation from triphenylcarbinol and tri-*p*-tolylcarbinol. Provisional values have been derived in a similar manner for the reactions of the chlorodiphenylcarbinols for which satisfactory vapor pressures were not obtained.

In this way the quantities required by Eq. 4 to convert the data of the condensed systems to the vapor phase have been measured or estimated for all but two of the reactions listed in Table I. Average values of the equilibrium constants together with the free energy appear in Table VII.

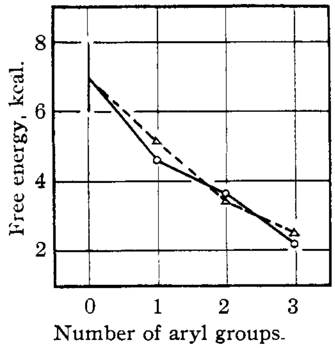

Fig. 3.—Free energy of vapor phase hydrolysis of arylchloromethanes at 60°: O, phenyl; Δ, *p*-tolyl.

In Fig. 3 the free energy is plotted against the number of aryl groups for the compounds in the two series containing entirely phenyl or *p*-tolyl radicals. The vertical line for the case where there are no aryl groups represents a free energy of 7000 ± 1000 cal., calculated from thermal and spectroscopic data for the reaction

$$CH_3OH(g) + HCl(g) = CH_3Cl(g) + H_2O(g)$$

The large uncertainty comes almost entirely from the heat of formation of methyl chloride.

Table VII

Vapor Phase Equilibrium Constants and Free Energy at 333°A. for the Reaction: $ROH(g) + HCl(g) = RCl(g) + H_2O(g)$

R	$K(1)$	$K(g)$	$-\Delta F^{\circ}_{33}$
Benzyl	2790	1220	4700
p-Xylyl	5660	2310	5130
Diphenylmethyl	371	247	3650
p-Methyldiphenylmethyl	365	210	3540
m-Methyldiphenylmethyl	409	228	3590
o-Methyldiphenylmethyl	432	298	3770
Di-*p*-tolylmethyl	235	180	3440
Di-*o*-tolylmethyl	669	..	..
p-Chlorodiphenylmethyl	301	182	3440
o-Chlorodiphenylmethyl	183	132	3230
p,*p*′-Dichlorodiphenylmethyl	222	155	3340
p-Phenyldiphenylmethyl	352	..	..
Triphenylmethyl	16.7	27	2180
Tri-*p*-tolylmethyl	32.5	52	2620

Although a probable error of 15% has been estimated for the vapor phase equilibrium constants of the reactions for which complete data have been obtained, it is improbable, because of the close similarity of the compounds studied, that the relative error between any two constants is much more than half of this value. In energy units, the corresponding uncertainty of 100 cal. compares favorably with the accuracy normally attained in thermal measurements. Fig. 3 shows a curious reversal between the phenyl and *p*-tolyl compounds which appears to be at least qualitatively correct, since it remains as a distinct irregularity after allowing for an optimum combination of probable errors. It is evident that no simple additive relations can be derived from the results.

Summary

Equilibrium constants have been measured at 60° for the conversion of fourteen mono-, di- and triarylcarbinols to chlorides in benzene solution through the action of aqueous hydrochloric acid.

For four of the reactions, vapor pressures of the carbinols and chlorides together with partial pressures of the solvent over their benzene solutions have been measured and applied to the calculation of the vapor phase equilibrium constants. Estimates of the vapor phase constants have been made for eight of the remaining reactions.

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