as a guide to the extent to which the ratio deviates from the ideal limiting value. Only those ratios having the same ideal value should be identical according to the restatement of the principle of specific interaction.

The fact that $(Mg/Cd)SO_4$ ratios for thallous iodate and lanthanum iodate are sensibly identical, *i. e.*, 0.938 and 0.939, is most gratifying. The $(SO_4/Cl)Mg$ ratios, however, are uniformly 1% lower than are the values previously reported by La Mer and Goldman.[1] Aside from possible inaccuracies in the determination of the solubilities, this is most likely to be ascribed to possible constant error in determining the chloride concentration of the solvents to be 0.1 *N* by the Mohr methods. Unfortunately we have not had an opportunity to repeat this phase of the work to establish the source of this 1% discrepancy. Granting, however, even this limit of uncertainty, it seems very improbable that the 8 and 11% differences in the (SO_4/Cl) Mg ratio as compared to the $(SO_4/Cl)Cd$ ratio for the two saturating salts can arise from analytical error alone. We therefore conclude that the specific interaction principle does not hold when considering such an atypical electrolyte as cadmium chloride, though in view of the marked abnormality which this salt exhibits it is surprising that the principle holds as well as it does.

NEW YORK, N. Y.

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

THE HYDROLYSIS EQUILIBRIA OF TRIPHENYLCHLOROMETHANE AND TRIPHENYLBROMOMETHANE. THE FREE ENERGY OF SOME REACTIONS OF TRIPHENYLCHLOROMETHANE, TRIPHENYLBROMOMETHANE AND TRIPHENYLCARBINOL

BY J. O. HALFORD

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The standard free energy of a reaction is related to the equilibrium constant by the familiar equation, $\Delta F^\circ = -RT \ln K$, and the two functions may be taken as alternative expressions of the tendency of the reaction to take place. However, the standard free energy is more significant, since it is related more directly to the fundamental properties of the substances involved in the reaction, and permits a wider application of the results. One advantage is that the intention to express results as free energies usually leads to experiments so carried out that the data may be applied not only to the reaction measured but to a number of related reactions as well. Certain difficulties may arise as a result, for with a given reaction the conditions most favorable to the production and measurement of equilibrium are not, in general, the best conditions for the determination of free energy relations. This is particularly true of organic equilibria, of which many are known, but few have been measured in such a way as to permit wide application of the results. Organic equilibria are usually established most readily in the liquid phase at high concentration and at elevated temperatures, while the best conditions for their interpretation in the more general form are dilute solutions in which reaction is very slow, and temperatures low enough to permit accurate regulation, sampling and analysis. The type of procedure to be employed and the method of interpretation of the results are illustrated by the work of Lewis and Burrows[1] on the free energy of urea, and that of Branch,[2] on the free energy of formic acid.

The reactions studied in this work have been selected as among the more rapidly established of the known organic equilibria, and it is suggested that for a given type reaction, experimental conditions will be determined most readily by studying first those cases which, regardless of complexity of structure of the compounds involved, will permit the simplest experimental procedure.

When a triaryl carbinol reacts with an acid, the resulting compound of the triarylmethyl with the acid radical may be a substance of the un-ionized type, such as triphenylchloromethane, or of the ionized type, such as triphenylmethyl sulfate. This has been discussed recently by Hantzsch and Buroway.[3] The type of molecule obtained depends on the nature of the acid and of the triaryl carbinol, and also upon the solvent employed. The two processes are represented by the following equations

$$R_3COH + HX = R_3CX + H_2O \qquad (1)$$

$$R_3COH + H^+ = R_3C^+ + H_2O \qquad (2)$$

The extent to which Reaction 2 takes place should be independent of the particular strong acid used, and is known to vary greatly with the triaryl radical involved. Triphenylcarbinol is converted to an ionized salt only by high concentrations of sulfuric and perchloric acids, while the methoxytriphenylcarbinols enter into this type of reaction in the presence of dilute aqueous solutions of any of the strong acids. Measurements of the basicity of the triaryl carbinols, as carried out by Lund and others,[4] are quantitative studies of this type of reaction.

Equation 1 is typical of the action of hydrochloric or hydrobromic acid on the more weakly basic carbinols, and apparently no analogous reaction with the strong oxygen acids is known. The extent to which this reaction takes place depends primarily on the stability of the compound R_3X, and although, as has been stated, a considerable amount of quantitative data is available on reactions of type 2, very little of

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[1] Lewis and Burrows, This Journal, **34,** 1515 (1912).

[2] Branch, *ibid.*, **37,** 2316 (1915).

[3] Hantzsch and Buroway, *Ber.*, **63,** 1181 (1930).

[4] Lund, This Journal, **49,** 1346 (1927); Baeyer and Villiger, *Ber.*, **35,** 1189 (1902).

specific information has been obtained on the tendency toward the production of the un-ionized type of molecule. It should be interesting to study the effect of substitutions in this case, to see if an increased tendency toward the production of the ionized salt is accompanied by a change in the tendency of the un-ionized substance to form.

The material presented in this paper includes the development of the method of measurement, its application to the equilibria in the formation and hydrolysis of triphenylchloromethane and triphenylbromomethane, and some results obtained by combining these data with other known thermal constants. The method of measurement takes into account the fact that a typically organic solvent, such as benzene, should be the best medium for the formation of the un-ionized substance, and the results will be more readily interpreted if conditions are such that the activity and free energy of the water and acid are known. With these points in mind, equilibrium was studied in a two-phase system, a benzene phase in which the triphenylcarbinol and triphenylhalogenomethane were dissolved, and an aqueous phase containing the acid.

A benzene solution containing a known concentration of the carbinol or carbinol halide was shaken in contact with an aqueous solution of the halogen acid of such a strength that at equilibrium measurable concentrations of carbinol and halide were produced. The concentration of halide was measured by titration with alkali in the presence of alcohol, and that of the carbinol was obtained by difference. In each case the aqueous layer was tested for the presence of the carbinol salt by neutralization and dilution, but no evidence of its formation was obtained.

The Hydrolysis of Triphenylchloromethane.—The results are summarized in Table I, in which the first column shows the initial concentration of triphenylcarbinol or triphenylchloromethane, and indicates the direction in which equilibrium was approached, the second the concentration, in weight per cent., of the acid in the aqueous layer, the third the concentration, in moles per 1000 g. of solvent, of triphenylchloromethane after reaction, the fourth and fifth the partial pressures of hydrogen chloride and water, taken from the "International Critical Tables,"[5] the sixth, the ratio $p(\mathrm{HCl})m(\mathrm{carbinol})/p(\mathrm{H_2O})m(\mathrm{chloride})$, and the last the time in days through which reaction was allowed to proceed. The reaction under these conditions is very slow and, since only one pair of solutions came to equilibrium, the results would be inconclusive except for the method of checking shown in the following paragraphs. The fact that equilibrium was reached only in the presence of the highest acid concentration suggests catalysis by the acid.

The equilibrium constant is taken as the mean of the two values obtained

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[5] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 301.

TABLE I

THE HYDROLYSIS OF TRIPHENYLCHLOROMETHANE IN BENZENE AT 25° BY AQUEOUS HYDROCHLORIC ACID

Initial solution	HCl, wt., %	m $(C_6H_5)_3CCl$	p (HCl), mm. Hg	p (H_2O), mm. Hg	K	Time, days
0.193 M $(C_6H_5)_3CCl$	21.65	0.110	0.56	12.9	0.032	15
	24.20	.158	1.75	11.2	.034	5
	25.90	.176	3.5	10.0	.034	4
	26.60	.172	4.3	9.5	.0523	3
0.206 M $(C_6H_5)_3COH$	24.20	.138	1.75	11.2	.077	7
	26.60	.185	4.3	9.5	.0514	4

with 26.6% acid. The data of Table I may be summarized as follows. For the reaction

$$(C_6H_5)_3CCl \text{ (in benzene)} + H_2O(g) = (C_6H_5)_3COH \text{ (in benzene)} + HCl(g);$$

$$K_{298} = 0.0518;\ \Delta F^\circ_{298} = 1755 \text{ cal.} \qquad (3)$$

Here the standard free energy refers to the gases at one atmosphere pressure and the solutes at equal concentrations or mole fractions.

The Hydrolysis of Triphenylchloromethane in the Presence of Solid Triphenylchloromethane and Triphenylcarbinol.—If a large excess of the solid phases is kept in contact with aqueous hydrochloric acid, the acid concentration should reach a definite equilibrium value which depends only on the temperature. In order to establish this equilibrium it is necessary to add to the system enough benzene or petroleum ether to give a non-aqueous reaction medium, and to start with a concentration of acid not far different from the equilibrium value, for relatively large quantities of the organic materials produce by reaction only small changes in the acid concentration. Apparent equilibria may be reached, due to coating of one of the solid phases, and a measurement is acceptable only when it has remained constant for several days after the addition of fresh portions of each of the solids. The hydrochloric acid solution which at 25° remains unchanged in contact with solid triphenylchloromethane and triphenylcarbinol was found to contain 24.82% of hydrogen chloride. Whence, for the reaction

$$(C_6H_5)_3CCl(s) + H_2O(g) = (C_6H_5)_3COH(s) + HCl(g);$$

$$K_{298} = 0.2195,\ \Delta F^\circ_{298} = 900 \text{ cal.} \qquad (4)$$

The Solubility and Free Energy of Solution of Triphenylchloromethane, Triphenylbromomethane and Triphenylcarbinol in Benzene.—In order to show the relation between Equations 3 and 4, the free energy of solution of each of the solids must be determined. This requires measurement of the solubility and of the change of activity with concentration from the working concentration to the saturated solution. This was effected by measuring the vapor pressure lowering of benzene by the solute. The solution was introduced into a bulb to which a closed arm mercury manometer had been sealed. The apparatus was evacuated repeatedly until consistent readings were obtained with a cathetometer sensitive to 0.2 mm. Meniscus correction was minimized by taking all readings, including that with pure benzene, against the same manometer, and making frequent observations of the character of the meniscus. The temperature was constant to 0.01°. The analysis for triphenylchloromethane or triphenylbromomethane, carried out after the measurement, depended on the acid produced by hydrolysis. Triphenylcarbinol was determined as residue after evaporation of the benzene. When the residue was dissolved in acetone and the evaporation repeated, a slightly smaller figure was obtained. This was accepted as correct. The pressure readings with triphenylbromomethane were not reproducible, and the depressions were about half as large as those calculated from Raoult's law. Table II shows the results of the measurements. The approximation to Raoult's law was sufficiently close, in the solutions of triphenylchloromethane and triphenylcarbinol, for the present purpose, and only a few measurements were required. The first column shows the substance, the second the mole fraction of the solute, the third the vapor pressure lowering, the fourth the value calculated from Raoult's law, and the last the solubility in g. per 100 g. of benzene.

TABLE II

SOLUTIONS OF TRIPHENYLCHLOROMETHANE, TRIPHENYLBROMOMETHANE AND TRIPHENYLCARBINOL IN BENZENE; SOLUBILITY AND VAPOR PRESSURE LOWERING AT 25°

Substance	N_2	Δp (mm. Hg.)	Δp (Raoult's law)	Solubility
$(C_6H_5)_3CCl$	0.1938	20.6	19.0	85.8
$(C_6H_5)_3CCl$	.0624	6.2	5.9	
$(C_6H_5)_3CBr$	.0843			39.5
$(C_6H_5)_3COH$	.0472	5.3	4.6	16.5

Since, for the equilibria under consideration, the deviations from Raoult's law tend to cancel, the free energy of each of the substances in solution is assumed to be a simple logarithmic function of the mole fraction. For the reactions

$$(C_6H_5)_3CCl(s) = (C_6H_5)_3CCl\text{ (in benzene, }N_2 = 0.0724\text{)};\ \Delta F^\circ_{298} = -576\text{ cal.} \quad (5)$$

$$(C_6H_5)_3COH(s) = (C_6H_5)_3COH\text{ (in benzene, }N_2 = 0.0724\text{)};\ \Delta F^\circ_{298} = 261\text{ cal.} \quad (6)$$

By combining Equations 4, 5 and 6, a check on Equation 3 is obtained. The value of the free energy is 1737 cal. sufficiently closely to justify the interpretation of the equilibrium data. In subsequent calculations the value 1750 will be used. By combining the above equations with the appropriate free energies from Lewis and Randall,[6] the results may be expressed in the following forms

$$(C_6H_5)_3CCl(s) + H_2O(l) = (C_6H_5)_3COH(s) + H^+ + Cl^-;\ \Delta F^\circ_{298} = -5722\text{ cal.} \quad (7)$$

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

$(C_6H_5)_3CCl$ (in benzene) + $H_2O(l)$ = $(C_6H_5)_3COH$ (in benzene) + $H^+ + Cl^-$;
$\Delta F^\circ_{298} = -4872$ cal. (8)

$(C_6H_5)_3CCl(s) + {}^1/_2O_2(g) + {}^1/_2H_2(g) = (C_6H_5)_3COH(s) + {}^1/_2Cl_2(g)$;
$\Delta F^\circ_{298} = -30,915$ cal. (9)

$(C_6H_5)_3CCl$ (in benzene) + ${}^1/_2O_2(g) + {}^1/_2H_2(g)$ = $(C_6H_5)_3COH$ (in benzene) + ${}^1/_2Cl_2(g)$;
$\Delta F^\circ_{298} = -30,065$ cal. (10)

The Hydrolysis of Triphenylbromomethane.—Constant boiling hydrobromic acid was found after two distillations to be sufficiently free from bromine. Preliminary measurements indicated that the optimum concentration was in the neighborhood of 41%, and this was readily obtained by diluting the constant boiling acid. Triphenylbromomethane was prepared by the action of acetyl bromide on triphenylcarbinol, and its analysis showed 99.6% purity. Benzene solutions of the carbinol and bromide containing 0.2 mole per 1000 g. of solvent were shaken with 41% hydrobromic acid. It was found necessary to exclude strong light from the reaction mixtures, because of a tendency to form triphenylmethyl peroxide and liberate bromine. This reaction will be discussed in another communication. Equilibrium was reached after fourteen days. The results are not as accurate as those with triphenylchloromethane, due mainly to the character of the available vapor pressure or activity data on strong solutions of hydrobromic acid. Starting with the triphenylbromomethane solution the equilibrium constant was 6.5×10^{-4}, and for the reverse reaction, 7.7×10^{-4}. For the reaction

$(C_6H_5)_3CBr$ (in benzene) + $H_2O(g)$ = $(C_6H_5)_3COH$ (in benzene) + $HBr(g)$;
$\Delta F^\circ_{298} = 4310$ cal. (11)

The error in the above result is probably not more than 100 calories.

The following forms of expressing the result are of interest

$(C_6H_5)_3CBr$ (in benzene) + $H_2O(l)$ = $(C_6H_5)_3COH$ (in benzene) + $H^+ + Br^-$;
$\Delta F^\circ_{298} = -5690$ cal. (12)

$(C_6H_5)_3CBr$ (in benzene) + ${}^1/_2O_2(g) + {}^1/_2H_2(g)$ = $(C_6H_5)_3COH$ (in benzene) +
${}^1/_2Br_2(l)$; $\Delta F^\circ_{298} = -37,660$ cal. (13)

Preparation of Triphenylchloromethane from Triphenylcarbinol.—The standard procedure effects the conversion by the action of acetyl chloride or dry hydrogen chloride on the carbinol in ether or benzene. The data of Equation 4 and Table II suggest the following modification. The carbinol and about twice the amount of benzene required to dissolve the chloride to be formed are placed in a flask or separatory funnel and an equal volume of concd. hydrochloric acid is added. The progress of the reaction may be observed as the mixture is shaken. The excess carbinol goes into solution in a few minutes. At this point the hydrochloric acid is drawn off and replaced, the shaking is continued for a few minutes and the benzene layer is separated and dried over calcium chloride. After drying, part of the benzene is removed by distillation on the steam-bath, and crystallization obtained by the addition of petroleum ether. Triphenylchloromethane melting at 112–113° was prepared from the carbinol by this procedure in 90% yield. A similar preparation in ether solution was carried out by Baeyer and Villiger.[7]

The Reaction of Triphenylchloromethane with Hydrogen Bromide and with Bromine.—Subtracting Equation 11 from Equation 3 shows the feasibility of replacing chlorine by bromine by the action of hydrogen bromide in benzene solution

$$(C_6H_5)_3CCl \text{ (in benzene)} + HBr(g) = (C_6H_5)_3CBr \text{ (in benzene)} + HCl(g); \quad \Delta F^\circ_{298} = -2560 \text{ cal.} \qquad (14)$$

This reaction will probably take place in either direction because of the ease with which a stream of gas from a generator will carry away the gas which is formed.[8]

For the reaction of triphenylchloromethane with bromine, from Equations 10 and 13

$$(C_6H_5)_3CCl \text{ (in benzene)} + {}^1/_2Br_2(l) = (C_6H_5)_3CBr \text{ (in benzene)} + {}^1/_2Cl_2(g); \quad \Delta F^\circ_{298} = 8080 \text{ cal.} \qquad (15)$$

showing a strong tendency for chlorine to replace bromine in the compound.

The Reaction of Triphenylchloromethane with Bromide Ion and with Metallic Bromides.—The equations follow

$$(C_6H_5)_3CCl \text{ (in benzene)} + Br^- = (C_6H_5)_3CBr \text{ (in benzene)} + Cl^-; \quad \Delta F^\circ_{298} = 820 \text{ cal.} \qquad (16)$$

$$(C_6H_5)_3CCl \text{ (in benzene)} + AgBr(s) = (C_6H_5)_3CBr \text{ (in benzene)} + AgCl(s); \quad \Delta F^\circ_{298} = 4282 \text{ cal.} \qquad (17)$$

$$(C_6H_5)_3CCl \text{ (in benzene)} + HgBr(s) = (C_6H_5)_3CBr \text{ (in benzene)} + HgCl(s); \quad \Delta F^\circ_{298} = 3940 \text{ cal.} \qquad (18)$$

Equation 16 states that in benzene solution in contact with an aqueous layer containing bromide and chloride ions at unit activity, equilibrium is established when the concentration of triphenylchloromethane is about three times that of triphenylbromomethane. According to Equation 17, if triphenylbromomethane in benzene is kept in contact with silver chloride, a 99.9% conversion to triphenylchloromethane should occur. This is consistent with the results of Gomberg and Cone, who found that the bromine in a number[9] of related compounds was replaced by this procedure.

The Relative Dissociation Tendency of Triphenylchloromethane and Triphenylbromomethane.—Equation 15 may be considered as the difference of two reactions of dissociation

$$(C_6H_5)_3CCl \text{ (in benzene)} = (C_6H_5)_3C + {}^1/_2\, Cl_2(g), \text{ and} \qquad (19)$$

$$(C_6H_5)_3CBr \text{ (in benzene)} = (C_6H_5)_3C + {}^1/_2Br_2(l) \qquad (20)$$

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[7] See Gomberg, *Ber.*, **35**, 2404 (1902).

[8] Straus, *Ann.*, **363**, 323 (1909).

[9] Gomberg, Ref. 7; Gomberg and Cone, THIS JOURNAL, **33**, 531 (1911).

Although the individual equilibrium constants are not known, the ratio K_{19}/K_{20} is the constant of Equation 15, namely 10^{-6}, indicating that under comparable conditions in benzene the dissociation of the bromide is 10^6 times that of the chloride.

Similarly, Equation 16 may be divided into two ionic dissociations

$$(C_6H_5)_3CCl \text{ (in benzene)} = (C_6H_5)_3C^+ + Cl^-, \text{ and} \tag{21}$$

$$(C_6H_5)_3CBr \text{ (in benzene)} = (C_6H_5)_3C^+ + Br^- \tag{22}$$

The interpretation in this case is less definite, because the free energies of aqueous chloride and bromide ions were used in the original equation, and the result is of more interest if applied to non-aqueous solutions. Strictly, it means that a benzene solution of triphenylbromomethane in contact with aqueous bromide ion at unit activity should produce in either phase three times the concentration of triphenylmethyl ions developed by an equally strong benzene solution of triphenylchloromethane in contact with aqueous chloride ion at unit activity. Since, however, the work of transferring bromide and chloride ions from one medium to another is probably about the same, one may conclude that in benzene, and probably in other solvents as well, triphenylbromomethane has the slightly greater tendency to dissociate into ions. The conductance measurements of Walden,[10] made in liquid sulfur oxide, show a difference somewhat larger than the factor of three which may be estimated from Equation 16.

Summary

1. Data are presented on the equilibria in the hydrolysis of triphenylchloromethane and triphenylbromomethane in benzene by aqueous hydrochloric and hydrobromic acids.

2. The solubilities of triphenylchloromethane, triphenylbromomethane and triphenylcarbinol in benzene have been measured, and some data on the lowering of the vapor pressure of benzene by these substances have been obtained.

3. The results, expressed as free energies, have been combined with other free energy data to give information about the reaction of triphenylchloromethane with hydrogen bromide, bromine, silver bromide and mercurous bromide. The relative tendencies of triphenylchloromethane and triphenylbromomethane to dissociate into ions and neutral molecules have been discussed.

Ann Arbor, Michigan

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[10] Walden, *Z. physik. Chem.*, **43**, 454 (1903).