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Some physico-chemical studies of organometallic and furan compounds

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SOME PHYSICO-CHEMICAL STUDIES OF

ORGANOMETALLIC AND FURAN COMPOUNDS

by

Willard E. Catlin

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In charge of Major Work

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ACKNOWLEDGMENT

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A. RELATIVE REACTIVITIES OF HALIDES

AND

SUPER-AROMATIC PROPERTIES OF FURAN

INTRODUCTION

Aromatic properties (1) are concerned not only with relative velocities of substitution and the behavior of atoms and groups attached directly to the nucleus, but also with the effect of the nucleus on lateral substituents. It has long been known that aromatic nuclei can exert a profound influence on the reactivity of some laterally situated halogens. Illustrations are the high reactivities of chlorine in compounds like benzyl chloride and benzoylmethyl chloride ($C_6H_5COCH_2Cl$).

Numerous methods have been proposed and used to establish the relative reactivities of halides. Semb and McElvain (2) have compared the reactivity of a number of alkyl bromides by means of their reaction velocities with piperidine. This reaction has the disadvantage of being accompanied by a number of side reactions, one of the principal being the removal of hydrogen and bromine from adjacent carbon atoms to form an unsaturated compound. Norris and Morton (3) have developed a

(1) Gilman and Towne, Rec. trav. chim., 51, 1054-1064 (1932).
(2) Semb and McElvain, J. Am. Chem. Soc., 53, 690-696 (1931).
(3) Norris and Morton, J. Am. Chem. Soc., 50, 1795-1803 (1928).

method for comparing the reactivity of halides by the reaction with alcohol to form the ether and hydrogen halide. The course of the reaction was followed by conductivity methods. It is obvious that under ordinary conditions this method is limited to quite reactive halides.

Haywood (4) has studied the comparative reactivity of a number of alkyl iodides by means of the reaction

$$C_6H_5CH_2ONa + RI \rightarrow NaI + C_6H_5CH_2OR$$
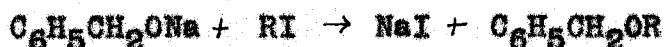
Other methods which have been used are the removal of hydrogen halide with alcoholic potash, the reaction with alcoholic silver nitrate, the reaction with sodium thiosulfate, and reactions with tertiary amines.

Unfortunately there is no complete agreement in the order of relative reactivities of a reasonable number of halides determined by any two methods. Furthermore, a series of relative reactivities determined by a selected method is frequently altered when the same method is used under different conditions. In short, there is no ideal series which can be applied rigorously to all reactions of halides, and the best which can be hoped for at this time is a series of relative reactivities which has a by and large usefulness.

(4) Haywood, J. Chem. Soc., 121, 1904-1921 (1922). References are given to numerous other methods which have been used in studies of comparative reactivities of halides.

The classical studies by Conant, Kirner and coworkers (5) on the relative reactivities of halides has provided a very convenient method for correlating the reactivities of many new halides with those previously investigated. The procedure consists in measuring the rate of the following metathetical reaction, absolute acetone being used as the solvent:

$$RX + KI \rightarrow RI + KX$$
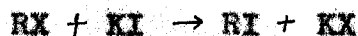
This reaction has the advantage of being free from side reactions such as hydrolysis and formation of unsaturated or cyclic compounds (5b). The reaction is probably between the iodide ion and the organic halide since the rate is essentially the same with sodium iodide and lithium iodide as with potassium iodide. The reaction velocity corresponds to that of a simple bimolecular reaction (5c).

(5) (a) Conant and Kirner, J. Am. Chem. Soc., 46, 232-252
        (1924);
    (b) Conant and Hussey, ibid., 47, 476-488 (1925);
    (c) Conant, Kirner and Hussey, ibid., 47, 488-501 (1925);
    (d) Kirner, ibid., 48, 2745-2753 (1926) and 50, 2446-
        2455 (1928); Kirner and Richter, ibid., 51, 3409-
        3418 (1929).
    See, also, Bennett and Berry, J. Chem. Soc., 130, 1676-
        1684 (1927) and Juvala, Ber., 63, 1989-2009 (1930).

EXPERIMENTAL

The procedure used was essentially that of Conant and Kirner. In the case of the more reactive (or unstable) halides such as benzoylmethyl chloride, 2-furfuryl chloride, 2-furoylmethyl chloride and 2-furoylmethyl bromide, an acetone solution of the halide was prepared and aliquot portions of this used in several determinations. The concentration of the reactants was thus reduced to one-half the usual value.

Because of the instability of the furfuryl halides in the presence of mineral acids, it was found advantageous to hydrolyze the reaction mixture with ice and water and extract with chloroform before adding the hydrochloric acid prior to the iodate titration. This made it much easier to obtain a satisfactory end point.

Calculations were made on the basis of the following form of the second order equation:

$$k = \frac{1}{t(r-1)b} \log \frac{r-x}{r(1-x)}$$

t = time in hours;

b = concentration of potassium iodide in moles per liter;

r = ratio of organic chloride to potassium iodide; and

x = fraction of potassium iodide reacted in time t.

The factor 2.303 was omitted in all cases.

The value of $k_{50°}$ was calculated for all those substances
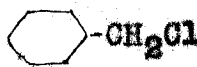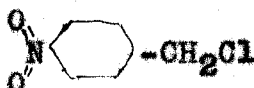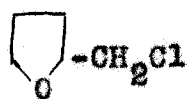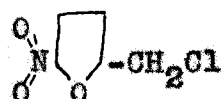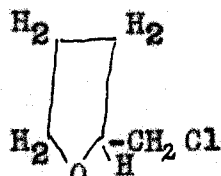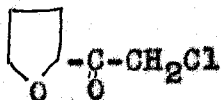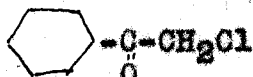
which were of such reactivity that they could not be measured at this temperature, with the aid of the equation

$$\log k_{50}o/\log k_t = A \left(\frac{1}{275 - t} - \frac{1}{323}\right).$$ A value of 4000 was used for A.

The relative reactivities (R) are based on an arbitrary value of one for n-butyl chloride after the convention of Conant and Kirner.

The technique was checked by determining the reaction velocities of benzyl chloride and benzoylmethyl chloride. The former, at 25°, gave an average value of .766 and the latter, at 0°, 20.2. The values of Conant and Kirner for these compounds were .774 and 22.4, respectively.

Table I

Relative Reactivity of Some Halides

Compound	k_{0°	k_{25°	k_{50°	k_{60°	R[a]
I. $CH_3(CH_2)_2CH_2Cl$	---	---	0.0402	0.101	1.
II. (cyclohexyl)-CH_2Cl	---	0.786	7.89	---	197.
III. O_2N-(ring)-CH_2Cl	---	5.03	55.1	---	1370.
IV. (furyl)-CH_2Cl	0.827	11.7	(128.)[b]	---	3184.
V. O_2N-(furyl)-CH_2Cl	3.42	46.7	(510.9)	---	12,708.
VI. (tetrahydrofuryl)H_2...-CH_2Cl	---	---	(0.00102)	0.0024	0.025
VII. (furyl)-$\overset{O}{\underset{\parallel}{C}}$-$CH_2Cl$	21.3	---	(3949.)	---	98,230.
VIII. (cyclohexyl)-$\overset{O}{\underset{\parallel}{C}}$-$CH_2Cl$	20.2	---	(3745.)	---	93,130.

(a) R = Relative reactivity at 50°, n-butyl chloride = 1.
(b) Values in parentheses were calculated assuming A = 4000.

Table I (Cont.)
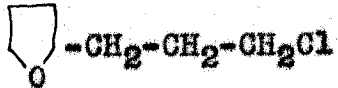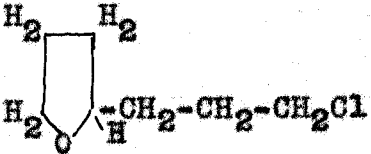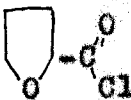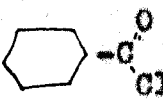
Compound	k_{0°	k_{25°	k_{50°	k_{60°	$R^{(a)}$
IX. [structure] $-CH_2-CH_2-CH_2Cl$	---	---	(0.101)	0.237	2.51
X. [structure] $-CH_2-CH_2-CH_2Cl$	---	---	(0.0535)	0.126	1.33

XI. [structure] $-C\overset{O}{\underset{Cl}{}}$ < XII. [structure] $-C\overset{O}{\underset{Cl}{}}$

Table II

Rates of Reaction of Some Halides with Potassium Iodide

2-Furfuryl Chloride (IV)

Time in hours	r	b	% reacted (100z)	$k_{25}°$
0.166	4.72	0.0216	37.2	12.4
0.25	4.72	0.0216	48.1	11.8
0.50	4.72	0.0216	66.0	10.1
0.25	4.56	0.0216	46.1	11.5
0.166	5.13	0.0195	35.8	12.7
0.50	5.13	0.0195	71.5	11.8
			Average	11.7

Cyclohexylmethyl Chloride

Time in hours	r	b	% reacted (100z)	$k_{60}°$
90	6.0	.0332	22.5	.0064
137	6.0	.0332	44.2	.0097
90	6.5	.0308	28.8	.0081
137	6.5	.0308	38.1	.0078
			Average	.0080

$k_{50}° = .0034$ (assuming A = 4000.)

R = 0.08

Table II (Cont.)

5-Nitrofurfuryl Chloride (V)
(r = 4.66, b = 0.0216)

Time in hours	% reacted	$k_{25°}$
0.0835	52.5	41.0
0.100	65.4	47.2
0.108	67.6	49.5
0.125	72.3	49.0
	Average	46.7

Tetrahydrofurfuryl Chloride (VI)
(r = 4.7, b = 0.0424)

Time in hours	% reacted	$k_{60°}$
84	8.7	0.0024
110	12.44	0.0026
167	15.8	0.0025
270	25.0	0.0024
	Average	0.0024

2-Furoyl Methyl Chloride (VII)
(r = 4.67, b = 0.0214)

Time in hours	% reacted	$k_{0°}$
0.0665	25.9	20.2
0.1666	55.0	22.3
0.325	74.4	20.4
	Average	21.3

γ-(2-Furyl)-Propyl Chloride (IX)
(r = 4.60, b = 0.0428)

Time in hours	% reacted	$k_{60°}$
2.16	20.3	0.236
11.5	67.5	0.236
12.15	70.5	0.240
	Average	0.237

γ-(2-Tetrahydrofuryl)-Propyl Chloride (X)
(r = 4.67, b = 0.0428)

Time in hours	% reacted	$k_{60°}$
5.25	25.3	0.125
8.0	37.2	0.131
9.0	39.7	0.139
16.25	59.2	0.128
	Average	0.126

Compounds

The 2-furfuryl chloride was prepared in accordance with the directions of Kirner (6), and check runs were made with two different batches of furfuryl chloride. The author is indebted to P. R. Van Ess for a part of the furfuryl chloride.

W. A. Zugschwert for the preparation of the 5-nitrofurfuryl chloride (7); W. O. Galloway for the preparation of the 2-furoylmethyl chloride; and to E. V. Brown for the 2-furoylmethyl bromide and 5-bromo-2-furoylmethyl bromide. Tetrahydrofurfuryl chloride was prepared by Kirner's method (8); and γ-(2-furyl)-propyl chloride and γ-(2-tetrahydrofuryl)-methyl chloride in accordance with Hewlett's directions (9). The benzoylmethyl bromide and p-bromobenzoylmethyl bromide were purchased from the Eastman Kodak Company.

(6) Kirner, J. Am. Chem. Soc., 50, 1955-1961 (1928) and 51, 3131-3135 (1929).

(7) Gilman and Burtner, Iowa State Coll. J. of Sci., 6, 399-394 (1932).

(8) Kirner, J. Am. Chem. Soc., 52, 3251-3256 (1930).

(9) Gilman and Hewlett, Rec. trav. chim., 51, 93-97 (1932).

DISCUSSION OF RESULTS

Correlations have been drawn between negativity and aromaticity (1) and it is to be expected, in general, that the reactivity of halogen in the series ACH_2X will increase with the negativity of the aromatic nucleus. On present evidence it has been suggested that furan is more aromatic than benzene. This finds support in this study of the relative reactivity of some halides containing the furan nucleus.

Furylalkyl Chlorides

An examination of the general results contained in Table I reveals that although benzyl chloride is 197 times as reactive as n-butyl chloride, the analogous 2-furfuryl chloride (compound IV) is about 3184 times more reactive than n-butyl chloride and more than 16 times as reactive as benzyl chloride. A related effect is observed when comparisons are made between p-nitrobenzyl chloride (III) and 5-nitro-2-furfuryl chloride (V), the furan compound being about 9 times more reactive than its benzene analogue.

As the distance between the phenyl group and the chlorine is increased by increasing the number of methylene groups, the activating influence of the phenyl group decreases rapidly. A related effect is apparent in the furan series, for γ -(2-furyl)-propyl chloride (IX) has a reactivity of 2.51 as compared to

1.72 for the corresponding phenyl derivative. It is obvious
that here, also, the 2-furyl radical has a greater activating
effect than the phenyl radical.

Tetrahydrofurylalkyl Chlorides

When the aromaticity of the furan nucleus is essentially
destroyed by complete nuclear hydrogenation there is a marked
drop in reactivity of lateral chlorine. The pronounced de-
crease in reactivity of chlorine in 2-tetrahydrofurylmethyl
chloride (VI) is probably due in part to the fact that the
chlorine is on a carbon atom which is in a β-position with
respect to oxygen in the saturated system. Kirner (10) has
observed qualitatively the relative inertness of the chlorine
in this compound toward hydrolysis, ether formation, and the
reaction with potassium iodide.

There is little doubt that the analogous cyclohexylmethyl
chloride (Table II) is of a somewhat higher order of reactivity,
as judged in part by the relative ease of Grignard reagent
formation as well as by the orienting studies on reaction
velocities with potassium iodide reported here.

A greater displacement of lateral chlorine from oxygen,
as in γ-(2-tetrahydrofurfuryl)-propyl chloride (X), increases
the relative reactivity from 0.025 to 1.33. This is an example

(10) Kirner, _J_. _Am_. _Chem_. _Soc_., _52_, 5251-5256 (1930).

of the very unusual case of an α-compound being less reactive
than the remaining members of the series. The α-tetrahydro-
furyl radical tends to depress the halogen reactivity below
that of saturated aliphatic halides instead of activating it
as do the phenyl and furyl radicals. As the number of methylene
groups is increased between the halogen and the tetrahydrofuryl
radical this influence decreases rapidly.

Furoylalkyl Chlorides

Phenacyl or benzoylmethyl chloride (VIII) is one of the
most reactive halides studied. A value of 93,130 was obtained
for this compound as compared to 98,230 for 2-furoylmethyl
chloride (VII). This difference is slight, and may be within
the experimental error which is of the order of 10 per cent,
but again indicates that the 2-furyl radical has a greater
activating effect than the phenyl radical.

The 2-furoylmethyl bromide and 5-bromo-2-furoylmethyl
bromide, as well as the analogous benzoylmethyl bromide and
p-bromobenzoylmethyl bromide (p-$BrC_6H_4COCH_2Br$), react prac-
tically instantaneously with potassium iodide in acetone at
0°, and so cannot be measured at this temperature.

Acid Chlorides

From some qualitative observations, 2-furoyl chloride
appears to be less reactive toward potassium iodide in acetone

than is benzoyl chloride. This may indicate that reactions
of acyl halides with potassium iodide involve preliminary or
concurrent reaction with the carbonyl group, for the carbonyl
group in 2-furfural, for example, is less reactive than the
carbonyl group in benzaldehyde (11).

Limits of Reactivities of Furan Halides

It is rather interesting to note the extremes in relative
reactivities of furan halides. 2-Furfuryl chloride may be
the most reactive simple chloride of the type ACH_2Cl (where A
designates an unsubstituted alkyl or aryl nucleus) which has
been allocated in a series of relative reactivities. In sharp
contrast is the relative inertness of 2-furyl chloride
$(2-C_4H_3OCl)$ and the astonishing inertness of 3-furyl chloride
(12). The simple halogenofurans are less reactive than the
corresponding halogenobenzenes, and 3-fluorofuran may be the
most inert simple fluoride. 2-Bromofuran can be dried over
metallic sodium. This compound showed no reaction with potas-
sium iodide in acetone in 23 days at 60°. However, bromobenzene
also appeared not to have undergone any measurable reaction in
18 days at 60°. These observations agree with those of Kirner
that the halogen in ACH_2X is more reactive than in AX or
$A(CH_2)_nX$, where A is a negative group. Where A is the tetra-
hydrofuryl (and probably also cyclohexyl) radical this is not
true.

. . . . . .

(11) Conant and Bartlett, J. Am. Chem. Soc., 54, 2881-2899 (1932).
(12) Gilman and Wright, J. Am. Chem. Soc., 55, 2893-2896 (1933).

The negativity (or aromaticity) of the radical appears to be the most important factor in the reaction of the halide with potassium iodide. This is likewise true in the scission of organometallic compounds with acids (see part D) and in the ionization of acids (see part C). However, negativity series based on these reactions would show numerous differences. The first two reactions are not equilibrium reactions and the driving force or decrease in free energy is only one of the factors, and not necessarily the determining factor in the reaction. Baker (13) suggests that the various anomalies in the effect of substituents on the reactivities of side-chain halogens may be explained by assuming the presence of at least two rate-determining stages of opposite polar character. It is obviously unsafe to draw conclusions as to electronic structure from studies of rates of reaction (14) unless a detailed analysis of the reaction mechanism has been made.

(13) Baker, J. Chem. Soc., 1933, 1128-1133. This is one of a concurrent series of theoretical papers on this subject. The other papers are by Bennett, Robinson, Shoppee, Ingold, and Dawson and Dyson.
(14) Adkins, J. Chem. Ed., 9, 1865-1873 (1932).

SUMMARY

1. The relative reactivities of some furan halides have been determined by a study of reaction velocities with potassium iodide in acetone.

2. The furan nucleus has a marked activating influence on halogens attached to a side chain. For example, 2-furfuryl chloride is about 16 times more reactive than benzyl chloride, and 5-nitro-2-furfuryl chloride is about 9 times more reactive than p-nitrobenzyl chloride, and about 12,700 times more reactive than n-butyl chloride. This effect decreases rapidly as the chlorine is placed at a greater distance from the ring; 1-furyl-3-chloropropane has only about twice the reactivity of the corresponding phenyl compound.

3. A halogen attached directly to the furan nucleus is comparatively inert.

4. The results are advanced in support of the concept that furan is more aromatic than benzene.

B. PARACHORS OF SOME FURANS

INTRODUCTION

Molecular volume has long been considered an additive function and considerable work has been done on the correlation of molecular volume and chemical constitution. Its practical value is, however, limited by a number of factors: It varies with the temperature. The actual volume occupied by the molecules is difficult to determine. The apparent volume is undoubtedly influenced by a variation in internal pressure from one liquid to another. This pressure, which for water is about 11,000 (1) atmospheres at ordinary temperatures, is produced by the forces of attraction between the molecules which give rise to surface tension. If a corrected volume could be determined which would take into account this contracting effect and which would not vary with temperature it should, even though empirical in nature, lead to more regularities than a comparison at constant temperature or constant vapor pressure.

The parachor is Sugden's attempt to invent such a function. MacLeod (2) has shown that in the equation $\gamma = C(D - d)^4$

(1) Sugden, J. Chem. Soc., 125, 1177-1189 (1924).
(2) MacLeod, Trans. Faraday Soc., 19, 38-42 (1923).

where γ = surface tension

D = density of liquid

d = density of vapor

for non-associating substances C is a characteristic constant which is independent of the temperature. By taking the fourth root of the above equation and multiplying by the molecular weight Sugden obtained his equation for the parachor:

$$P = \frac{M\gamma^{\frac{1}{4}}}{D - d} = CM$$

The quantity $\frac{M}{D-d}$ has dimensions of volume and at low temperatures, where d is small, is the (apparent) molecular volume; hence a comparison of P for different substances is, in the words of Sugden (1), "a comparison of the molecular volumes at temperatures at which the liquids have the same surface tensions". Sugden has also shown that, for most compounds, the parachor has a more or less definite relationship to the critical volume; namely 78 per cent ± 3 per cent.

The observed figures for P can be reproduced by adding together two sets of constants, one for the atoms in the molecule, the other for constitutional influences of unsaturation and ring closure. Position isomerism does not, in general, cause a change in P. A $>C=C<$ double bond has the same value as the $>C=O$ and $-N=O$ double bond. The same six-membered ring constant can be used for benzene, cyclohexane, pyridine and quinoline. The same triple bond constant is used for acetylenic compounds and nitriles.

The additive character of the parachor sets obvious limits to its application to problems of chemical constitution. A change in the position of a radical or linkage in the molecule has no effect on the value of this constant. If, however, two isomeric substances differ in structure by the replacement of a double bond by a ring, they should exhibit differences in parachor which will depend on the number of atoms in the ring.

The parachor has been used with distinct success in the study of certain types of valencies, notably singlet linkages and semipolar double bonds (3).

Although there is no present definite information concerning the constitution of furan the following forms and their electronic modifications are particularly useful (4):

$$P = 160.1 \qquad P = 157.1$$
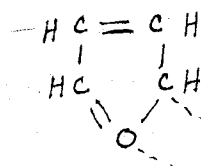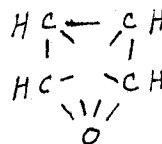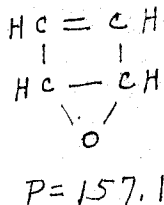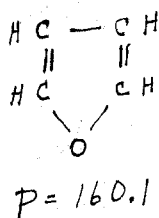
(The parachors given are those calculated using the atomic and structural values given in Table I.)

(3) Sugden, "The Parachor and Valency", London, 1930.
(4) See (a) Gilman and Wright, Chem. Reviews, 11, 324-327 (1932) and Gilman, Burtner and VanderWal, Rec. trav. chim., 52, 151-155 (1933) for a general discussion of these and other formulas proposed for furan, and (b) Pauling and Sherman, J. Chem. Phys., I, 606-617 (1933).

It appeared that a study of the parachors of some typical furans would not only throw some light on the constitution of furan, but would also assist in explaining the constitution of some substituted furans like 2-nitrofuran and compounds with the dynamic furfuryl linkage.

The results here reported are in support of the classical diolefinic formula (I) or structures related to it like centric formula (III). The ethylene oxide formula (II) is useful in interpreting some reactions like oxidation; however the compound represented by this formula is probably not present to a significant extent. It is, of course, impossible within the limits of accuracy for measuring parachor to definitely and rigorously exclude any formula. The best that can now be hoped for is an idea of predominant forms. It still appears altogether probable that furan consists of a dynamic equilibrium of a number of structures, some of which are more useful than others in interpreting specific reactions.

EXPERIMENTAL

The surface tensions (γ) were determined by the bubble pressure method described by Sugden (3) (5). Liquid densities (D) were determined with the usual picnometer in preference to the special picnometer described by Sugden (3). The latter method is less tedious but appears to give somewhat less dependable results. Densities of the vapors (d) were omitted except in the cases of furan, 2-methylfuran, 2,5-dimethylfuran, 2-bromofuran and 2-furfuryl methyl ether. In these cases (d) was still small enough to be calculated satisfactorily by the method of Sugden (3).

For calculating the parachor the usual formula $P = \dfrac{M \gamma^{\frac{1}{4}}}{D - d}$ was used, where M represents molecular weight.

All of the compounds, except nitrofuran, were freshly distilled prior to use, the furan, 2-methylfuran and 2,5-dimethylfuran being distilled from sodium. Nitrofuran was recrystallized from petroleum ether and dried in a vacuum desiccator.

The calculated values given in Table II are on the basis of a diolefinic structure (I). The atomic and structural parachors used in these calculations are given in the following table.

(5) Sugden, J. Chem. Soc., 125, 27-31 (1924).

Table I (6)

Some Atomic and Structural Parachors

Carbon	7.2	Single bond	0
Hydrogen	16.2	Double bond	20
Oxygen	20.0	Semipolar double bond	0
Bromine	68.0	Singlet link	- 10
Nitrogen	15.0	Triple bond	42
		3-membered ring	14.0
		4-membered ring	9.5
		5-membered ring	6.5
		6-membered ring	4.5
		7-membered ring	3.0

Corrections

OH group	-5.0
O_2 in esters	+2.0
NH_2, NHR or NR_2	+3.0
R_2C in 3-membered ring	-3.0

(6) Unpublished communication. Professor S. Sugden (Birk-beck College, University of London, London, England) to Henry Gilman. August 21, 1934.

Table II

Parachors of some Furans

Compound	(a) Furan	2-Methyl-furan	2,5-Dimethyl-furan	(b) 2-Bromo-furan	(c) 2-Nitro-furan
t (°C.)	20	20 30 40 50	20 30 40 50	20	30 40 50
D	0.9376	0.9158 0.9037 0.8917 0.8796	0.8962 0.8855 0.8744 0.8634	1.6500	1.3266 1.3137 1.3020
d	0.0017	0.0007 0.0009 0.0013 0.0019	0.0003 0.0004 0.0006 0.0008	0.0004	
γ	23.76	24.54 23.28 22.29 21.17	25.64 24.07 22.97 21.84	32.19	44.48 43.21 41.98
(P) obs.	160.4	199.4 199.5 200.1 200.4	241.2 240.2 240.5 240.6	212.6	220.1 220.5 220.9
(P) obs. mean	160.4	199.8	240.6	212.6	220.8
(P) calcd.	160.1	199.7	239.3	211.9	218.9
(P) obs. minus (P) calcd.	0.3	0.1	1.3	0.7	1.9

(b) Prepared in accordance with the directions of Shepard, Winslow and Johnson, J. Am. Chem. Soc., 52, 2083-2090 (1930). The density used was that reported by them.

(c) In the case of materials boiling above 150° the density of the vapors was negligible at the temperatures used.

Table II (Cont.)

Compound	2-Furfuryl Alco-hol ("water soluble form")	2-Furfuryl Alcohol (d) ("water insoluble form")	2-Furfuryl Methyl Ether
t (°C.)	20 30 40 50	20 30 40 50	15 25 35 45
D	1.1331 1.1239 1.1145 1.1052	1.1347 1.1258 1.1166 1.1076	1.0288 1.0177 1.0082 0.9967
d			0.0001 0.0002 0.0002 0.0003
γ	39.37 38.44 36.99 36.07	39.35 37.58 37.00 35.94	33.27 31.66 30.14 28.78
(P) obs.	216.6 217.1 216.8 217.3	216.2 215.5 216.4 216.6	261.5 261.1 260.3 260.4
(P) obs. mean	216.9	216.2	260.8
(P) calcd.	214.7		259.3
(P)obs. minus (P) calcd.	2.2		1.5

(d) The preparation of the so-called water insoluble form of
2-furfuryl alcohol is sometimes erratic. The particular
specimen used here was prepared by shaking 100 g. of
freshly distilled, water soluble form with 100 cc. of
water to which had been added 2 drops of conc. hydro-
chloric acid. The "insoluble" form began to separate
after 24 hours, and subsequent to standing for 3 weeks
it was removed and found to distil at $75-77°/14$ mm. It
was somewhat soluble but not miscible with water at room

temperature, and its instability (reflected in a blackening and change to a thick viscous mass) may possibly have been due to a trace of hydrochloric acid. Molecular weights were 102, 103 and 105, 105 on two different preparations; calcd. for monomolecular 2-furfuryl alcohol, 98.

Table II (Cont.)

Compound	2-Tetrahydro-furfuryl Ethyl Ether	2-Furfuryl 2-Furoate	Ethyl 2-Furoate	2-Furfuryl 2-Furoate
t (°C.)	15 / 25 / 35 / 45	15 / 25 / 35 / 45	40 / 50 / 60 / 70	20 / 30 / 40 / 50
D	0.9456 / 0.9342 / 0.9249 / 0.9152	1.1628 / 1.1541 / 1.1441 / 1.1349	1.0972 / 1.0867 / 1.0765 / 1.0651	1.2409 / 1.2309 / 1.2200 / 1.2102
d				
γ	29.25 / 28.35 / 27.51 / 26.41	45.59 / 42.46 / 41.60 / 39.48	34.44 / 33.31 / 32.25 / 31.01	44.03 / 42.74 / 41.07 / 40.29
(P) obs.	320.4 / 321.1 / 321.9 / 322.0	212.2 / 212.5 / 213.1 / 212.2	309.1 / 309.5 / 310.0 / 309.8	398.5 / 398.8 / 398.6 / 399.8
(P) obs. mean	321.3	212.5	309.6	398.9
(P) calcd.	323.7	207.3	304.5	392.6
(P) obs. minus (P) calcd.	-2.4	5.2	5.1	6.3

DISCUSSION OF RESULTS

The difference between the calculated parachors of the diolefinic form (I) and the ethylene oxide form (II) is 160.1 - 157.1 = 3.0. It is significant that in no case does the observed parachor fall below the value calculated on the basis of formula (I). The 2-tetrahydrofurfuryl ethyl ether may be ignored in this connection since it does not contain a furan nucleus.

Those particular discrepancies which may be beyond experimental error are with compounds having groups laterally unsaturated and conjugated with a diolefinic nucleus, particularly carbonyl. The customary correction (see Table I) of -2.0 for oxygen in esters was used, for it is generally agreed that esters afford one of the best illustrations of constitutive influences in parachor and this correction is probably warranted on the basis of present knowledge. It is interesting to observe that had the correction for oxygen in esters been omitted the calculated values would have been much more in favor of the diolefin structure, as calculated, and still well above that for the ethylene oxide form.

If the carbonyl containing compounds such as 2-furfural and the esters had any large quantity of the semipolar form present /and the carbonyl group might function as a semipolar

linkage on the basis of resource energies (4b)7, the observed parachor might be expected to be lower than the calculated value. It was found to be higher.

The calculations with 2-nitrofuran were made on the customary basis of a semipolar linkage in the nitro group.

Parachors were not calculated for formulas (III) or (IV) but if the centric bond was assumed to have a value of zero like any single bond the parachor for the centric formula (III) would be 120.1, which is very much lower than any of the observed figures.

Sugden (7) says: "Formulas (III) and (IV) involve improbable valencies for oxygen. . .(Quadrivalent oxygen has special properties which are not found in these compounds.)"

The Raman spectra of parent nuclei having pronounced aromatic characteristics indicate the absence of double bonds, and that such double bonds are developed or stabilized with the introduction of lateral groups (8).

(7) Unpublished communication. Professor S. Sugden (Birkbeck College, University of London, London, England) to Henry Gilman. May 12, 1934.
(8) Bonino, Z. Physik. Chem., B22, 21-44 (1933) and Glockler and Wiener, J. Chem. Phys., 2, 47 (1934).

SUMMARY

The determination of the parachors of a number of typical furans shows that the classical diolefin structure is to be preferred to the ethylene oxide structure. However, the parachor does not exclude the probability of furans being a dynamic equilibrium mixture of several forms.

C. IONIZATION CONSTANTS OF SOME ACIDS OF THE FURAN SERIES

AND

SUPER-AROMATIC PROPERTIES OF FURAN

INTRODUCTION

The negative character of the furan nucleus has been described in terms of the relative ease of splitting of mixed organolead compounds (1); ease of substitution in the furan nucleus (2); and relative reactivity of halides (3).

A further manifestation of the activating influence of the furan nucleus is to be found in the strength of the carboxylic acids as compared to the corresponding acids of the benzene series (4).

When an atom or group of atoms is substituted in the compound RCO_2H to give $R'CO_2H$, the ionization constant is raised or lowered in a degree which depends upon: the negativity of the entering group (5); steric effects of the entering group (6);

(1) Gilman and Towne, Rec. trav. chim., 51, 1054-1064 (1932).
(2) Gilman and Young, J. Am. Chem. Soc., 56, 464-466 (1934).
(3) See page 19.
(4) For the effect of nuclear substituents on the ionization of benzoic acid see Kuhn and Wassermann, Helv. Chim. Acta, 11, 3-50 (1928).
(5) Lewis, J. Am. Chem. Soc., 38, 762-785 (1916).
(6) Flürscheim, J. Chem. Soc., 1928, 3039-3040.

distance of the entering group from the $-CO_2H$ group (7);
and the negative properties of the original R group.

The negativity is the ability of an atom or group to
attract electrons. A negative group increases the strength
of the acid in which it is substituted.

The effect of the substituted group falls off rapidly
(usually as an exponential function) as its distance from the
carboxyl group is increased.

Bulky groups adjacent to the carboxyl do not appear to
affect the process of ionization but tend to prevent the re-
verse process; thus steric hindrance increases the ionization
constant.

The introduction of a negative atom or group into an
electrically neutral group always has a more pronounced effect
than a like introduction into a negative radical; i.e. the
replacement of one hydrogen in acetic acid by chlorine has a
greater relative effect than the replacement of a second which,
in turn, has a greater effect than the replacement of the
third. Similarly the introduction of a chlorine in benzoic
acid makes a greater proportional increase in the ionization
constant than a like introduction in the more negative furan
nucleus of furoic acid. In an analagous manner the introduc-
tion of a neutral methyl group will have a greater tendency to

(7) MacInnes, J. Am. Chem. Soc., 50, 2587-2595 (1928).

decrease the ionization constant of furoic than that of benzoic acid, and will have very little effect on the saturated aliphatic acid having six carbon atoms.

The increase in acidic strength from benzoic through thiophene-2-carboxylic to 2-furoic acid places these radicals in the same order of (increasing) negativity or aromaticity as the work of Gilman and Towne (1) on the scission of the aryllead compounds by hydrogen chloride. The 3-furyl radical has not been studied by the latter method. Its dissociation constant is only slightly greater than that of benzoic acid (see Table I).

The ionization constant has an inherent advantage over methods which depend upon rates of reaction as criteria of negativity or aromaticity in that it represents an equilibrium reaction.

The following table illustrates the change in ionization constants of the acids as R becomes more aromatic in character.

Table I

Ionization Constants of some Carboxylic Acids

Acid	$K \times 10^5$ (25°C.)
Acetic (8)	1.75
Benzoic (9)	7.3
Thiophene-2-carboxylic (10)	34.2
Thiophene-3-carboxylic (10)	7.8
Furan-2-carboxylic (11)	75.3
Furan-3-carboxylic	11.3

(8) Harned and Ehlers, J. Am. Chem. Soc., 55, 652-656 (1933).
(9) A value of 6.7 x 10⁻⁵ is reported by Kolthoff and Bosch, J. Phys. Chem., 36, 1695-1701 (1932).
(10) A value of 31.6 x 10⁻⁵ is reported for thiophene-2-carboxylic acid by Voerman, Rec. trav. chim., 26, 293-310 (1907).
(11) A value of 76 x 10⁻⁵ is reported by White and Jones, Am. Chem. J., 44, 159-199 (1910).

EXPERIMENTAL

A weighed quantity of the pure dry acid (12) was dissolved in distilled water which had been previously boiled to expel dissolved carbon dioxide. The solution was divided into two equal portions and one portion was titrated with carbonate-free sodium hydroxide, using phenolphthalein as the indicator. The quantity of acid used was such that in all cases the normality of the combined acid and salt was 0.01 (0.005N salt and 0.005N free acid). The half-neutral solution was placed in a thermostat at $25° \pm 0.2°$ and after the solution reached constant temperature (one-half hour or longer) the pH was determined with the quinhydrone electrode (with a bright platinum electrode about 1 cm. square) and saturated calomel electrode, using a saturated potassium chloride bridge.

A Leeds and Northrup student type potentiometer was used. The standard cadmium cell was checked against a Bureau of Standards cell and the whole set-up was checked daily against a standard buffer solution (0.05 molar potassium acid phthalate pH = 3.97).

The potassium acid phthalate was prepared by the method

(12) The author is indebted to R. J. VanderWal, G. F. Wright, H. R. Mallory and A. P. Hewlett for the preparation of the halogenated furoic acids; to R. R. Burtner for the 3-furoic acid; to R. A. Franz and R. R. Burtner for the methylfuroic acids; and to R. V. Young for the 5-nitrofuroic acid.

described by Clark (13). The quinhydrone was prepared by the method described by Grant (14).

For the half cells (13):

KCl (sat.), HgCl|Hg   E = 0.2458   at 25°

||(H$^+$) = 1, quinhydrone|pt   E = 0.6992   at 25°

$$\triangle E = 0.4534$$

$$pH = \frac{0.4534 - E \text{ observed}}{.0591} \quad \text{at } 25°$$

For the dissociation HAc = H$^+$ + Ac$^-$

$$K = \frac{(H^+)(Ac^-)}{HAc}$$

$$= \frac{(H^+)(salt + H^+)}{(Free\ acid - H^+)} = \frac{(H^+)(0.005 + H^+)}{(0.005 - H^+)}$$

(13) Clark, "The Determination of Hydrogen Ions", Third Edition, p. 193, Baltimore. 1928.

(14) Grant, "The Measurement of Hydrogen Ion Concentration", p. 48, London. 1930.

Table II

Ionization Constants of some Substituted Furoic Acids

Acid	M.P.($^{\circ}$C.)	E	pH	$c_{H^+} \times 10^5$	$K \times 10^5 (25^{\circ})$
3-Chloro-2-furoic	143-145	0.2815	2.909	123.4	204.1
5-Chloro-2-furoic	177-178	0.2755	3.010	97.72	147.4
5-Bromo-2-furoic	185-187	0.2754	3.012	97.28	144.5
5-Iodo-2-furoic	192-193	0.2713	3.081	83.0	116.0
3,4-Dichloro-2-furoic	168-170	0.2918	2.734	184.5	400.3
3,5-Dichloro-2-furoic	155-157.5	0.2910	2.748	178.7	377.4
4,5-Dichloro-2-furoic	197-197.5	0.2847	2.854	139.9	248.6
3,5-Dibromo-2-furoic	167-168	0.2889	2.783	164.8	326.8
5-Nitro-2-furoic	183	0.3012	2.575	266.0	870[a]
5-Methyl-2-furoic	107	0.2479	3.477	33.34	38.12
2-Methyl-3-furoic	100-101	0.1853	4.537	2.904	2.94
2,4-Dimethyl-3-furoic	122	0.1840	4.559	2.761	2.79
2,5-Dimethyl-3-furoic	134-135	0.1790	4.643	2.275	2.296
Mucobromic	121-122	0.2000	4.287	5.155	5.26
Furylacrylic	141	0.1920	4.423	3.776	3.83
2-Furoic	130-131	0.2627	3.227	59.30	75.2
3-Furoic	120	0.2190	3.966	10.82	11.30
Thiophene-2-carboxylic	126.5	0.2455	3.518	30.34	34.26

(a) Approximate (the method is most accurate for weak acids).

DISCUSSION OF RESULTS

Furan-3-carboxylic Acid (Table I)

Furan-3-carboxylic acid lies between furoic and benzoic acid in strength, but only slightly above the latter. The 3-position in furan has other characteristics which are more closely related to benzene than are those of the 2-position; such as ease of substitution, rate of hydrolysis of the ester, and probably the rate of scission of the organometallic compounds. It is of interest to note that the ratio of the strengths of the 2-acid and the 3-acid is of the same order of magnitude in furan and thiophene.

Methylfuroic Acids (Table II)

All of the methyl-2- and 3-furoic acids examined were found to be much weaker than the simple parent acids. It is to be expected that the presence of one or more alkyl side chains would decrease the very strong negative properties of the furan nucleus. The effect must be electronic and not steric since the latter effect would tend to increase the ionization constant when the methyl group is adjacent to the carboxyl group.

5-Nitrofuroic Acid (Table II)

The strongly negative nitro group produces a profound increase in the strength of the acid.

Furylacrylic Acid (Table II)

The furan ring, like any other negative or activating group, decreases rapidly in effect as its distance from the reactive group is increased. Furylacrylic acid is only slightly stronger than cinnamic acid. The ionization constants of these acids are 3.83×10^{-5} and 3.6×10^{-5} (15), respectively.

Halogeno-furoic Acids (Table II)

The 5-chloro- and 5-bromofuroic acids are of almost exactly the same strength. The 5-iodofuroic acid is somewhat weaker. The 3-chloro- is much stronger than is the 5-chlorofuroic acid due to the smaller distance between the chlorine and the carboxyl group.

Since the increase in the logarithm of the ionization constant of an organic acid caused by the introduction of a halogen is a function of the distance of the halogen from the carboxyl group (7), these constants should be of value in

(15) Scudder, "Conductivity and Ionization Constants of Organic Compounds", New York. 1914. Both of these acids are probably of the trans modification. The ionization constant of the cis acid is usually higher than that of the trans.

attempts to establish the structures of halogenated acids
(see Table III). In calculating -Log K for the supposed
2,5- and 4,5-dichlorofuroic acids it was assumed that the in-
crease in Log K due to a substituted halogen was an additive
constant which was characteristic of the position of substitu-
tion. This assumption is not strictly true since the intro-
duction of a second halogen will have less effect than the
introduction of the first. For this reason the predicted
values of -Log K should be (and are) lower than the experimental
values but the difference appears to be of a smaller order than
the difference between the actual values of the two acids.

It is still an open question whether these polar effects
are transmitted through the intervening carbon atoms or through
space (7). We might conceive of a puckered furan ring in which
the halogen in the 4-position is closer than that in the 3-
position to the carboxyl in the 1-position. Such a condition
is improbable due to the mutual steric and electrostatic repul-
sion of the two negative groups. This repulsion appears to be
strong enough in case of the dibasic (16) and chlorine substi-
tuted aliphatic acids to produce a straight or zig-zag chain
so that no five carbon periodicity is shown in the ionization
constants. None of the simple substituted furoic acids has
been resolved.

(16) Ingold, J. Chem. Soc., 1931, 2153-2169.

Mucobromic Acid (Table II)

The relatively low ionization constant of mucobromic acid is probably due to its existence in the lactonic form (17):
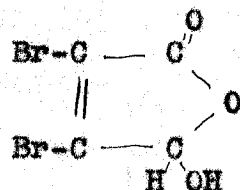
Table III

Correlation of Ionization Constants with Structure

Acid	M.P. ($^{\circ}$C.)	-Log K	$\triangle$	-Log K (Predicted)
2-Furoic	130-131	3.125		
3-Chloro-2-furoic	143-145	2.690	0.435	
5-Chloro-2-furoic	177-178	2.831	0.294	
3,4-Dichloro-2-furoic	168-170	2.398	0.292	
3,5-Dichloro-2-furoic	155-157.5	2.423		2.396
4,5-Dichloro-2-furoic	197-197.5	2.604		2.541

$\triangle$ = Increase in Log K due to chlorine in the 3-, 5-, and 4-positions, respectively.

(17) Hill, Widtsoe and Dunlap, Am. Chem. J., 19, 627-649 (1897).

Table IV

Correlation of Ionization Constants with

Rates of Alkaline Hydrolysis of Esters

Acid	Ionization Constant x 10^5	Hydrolysis Constant of Ethyl Ester (18)	Decarboxylation Temperature (19)	m.p.
2,4-Dimethyl-3-furoic	2.79		129	122
2-Methyl-3-furoic	2.94	.0176	101-103	101°C
Benzoic	6.7	.049 (20)		121°C
3-Furoic	11.3	.07[a]	152	120
5-Methyl-2-furoic	38.12	.075	122-125	107
2-Furoic	75.3	.22	158	131
5-Iodo-2-furoic	116.			
5-Bromo-2-furoic	144.3	.836	177-179	
5-Chloro-2-furoic	147.4	.855	180-182	
3,5-Dibromo-2-furoic	326.8	5.08	174	
3,5-Dichloro-2-furoic	377.4		168-170	
5-Nitro-2-furoic	870.		201-203	

(a) This value is only approximate.

(18) Gilman and Bradley, unpublished work.
(19) Gilman and Bradley, Iowa State Coll. J. Sci., 7, 429-431 (1933).
(20) Kindler, Ann., 450, 1-20 (1926).

From the preceding table it appears that the rate of hydrolysis of the ester depends upon the strength of the acid. Kindler (20) (21) and Hammett (22) have pointed out that this relationship is not constant over a wide range of compounds unless a correction is made for steric or "ortho" effects. Steric hindrance increases the ionization constant and decreases the rate of hydrolysis of the ester.

There appears to be little relationship between decarboxylation temperature and strength of acid.

(21) Kindler, Ann., 452, 90-120 (1927); ibid., 464, 278-292 (1928).
(22) Hammett and Pfluger, J. Am. Chem. Soc., 55, 4079-4089 (1933).

Table V

Correlation of Ionization Constants with Comparative
Reactivity of the Halides having the Same
Number of Carbon Atoms

Acid	K x 10^5	Halide	Comparative Reactivity
Propionic	1.35	n-Propyl chloride	1.03
Butyric	1.6	n-Butyl chloride	1.
3-Phenyl propionic	4.25	3-Phenyl-1-chloropropane	1.72
Phenyl acetic	5.4	2-Phenyl-1-chloroethane	1.12
Acrylic	5.6	Allyl chloride	79.
p-Bromobenzoic	6.6	p-Bromobenzyl chloride	48,100.
Benzoic	6.7	Benzyl chloride	197.
p-Chlorobenzoic	9.3	p-Chlorobenzyl chloride	533.
m-Nitrobenzoic	34.5	m-Nitrobenzyl chloride	780.
p-Nitrobenzoic	40.1	p-Nitrobenzyl chloride	1,370.
Furoic acid	75.	Furfuryl chloride	3,199.
o-Bromobenzoic	145.	o-Bromobenzyl chloride	77,300.
o-Nitrobenzoic	615.	o-Nitrobenzyl chloride	1,800.
5-Nitrofuroic	870.	5-Nitrofurfuryl chloride	12,624.

The comparative reactivities of the halides (with the exception of the furan derivatives) are those of Conant and coworkers. For references see page 7. The ionization constants are from Scudder, "Conductivity and Ionization Constants of Organic Compounds", New York, 1914.

As can be seen from the preceding table there is a quali-
tative agreement between the effect of the radical R on the
strength of the acid RCO_2H and the reactivity of the halide
RCH_2Cl. The most notable exceptions are among the ortho-sub-
stituted benzyl chlorides. Both the ortho- and parabromobenzyl
chlorides have an unexpectedly high reactivity while the ortho-
nitrobenzyl chloride is less reactive than would be expected.

Correlation with the Kharasch Series of Reactivities

Kharasch (23) places the aliphatic radicals below benzene
in negativity and would very probably place furan and thiophene
above benzene; but among the substituted radicals the agreement
between the Kharasch series and any series based on ionization
constants or reactivity of halides seems to be less satisfactory.
According to Kharasch the substitution of a chlorine in the
benzene ring makes it more positive, i.e., less reactive. On
the basis of ionization constants of acids or reactivity of
halides the introduction of a halogen always makes the parent
radical more negative in character.

(23) Kharasch and Flenner, J. Am. Chem. Soc., 54, 674-692
(1932).

SUMMARY

1. The ionization constants of 3-furoic acid and a number of substituted 2- and 3-furoic acids have been determined.

2. The results show the furan nucleus to be markedly more aromatic than the benzene nucleus.

3. The 2-furyl nucleus is more aromatic than the 3-furyl nucleus.

4. The strength of the acid RCO_2H has been correlated with the rate of hydrolysis of the ester RCO_2Et and the reactivity of the halide RCH_2X.

D. RELATIVE REACTIVITY OF SOME ORGANOMETALLIC COMPOUNDS

INTRODUCTION

In a qualitative manner there is a fair general agreement between the reactivity of the organometallic compounds and the position of the metal in the periodic table.

As might be expected the alkyl and aryl derivatives of the alkali metals are the most reactive (1). These compounds are highly polar in character and will conduct an electric current when dissolved in the proper medium (2). They react vigorously with oxygen, carbon dioxide and other compounds containing the carbonyl group, compounds having active hydrogens, and compounds containing halogens; and in some cases they split ethers. Because of the highly positive character of the metal, exchange reactions take place with hydrocarbons having a more negative R group (3). The rubidium and cesium compounds appear to be more reactive than those higher in the group.

The organometallic compounds of the second group elements

(1) For a general review and references see: Julius Schmidt, "Organometallverbindungen", Stuttgart. 1934.
(2) Hein, Petzchner, Wagner and Segitz, Z. Anorg. Allgem. Chem., 141, 161-227 (1924).
(3) Conant and Wheland, J. Am. Chem. Soc., 54, 1212-1221 (1932).

are, in general, less reactive than the organoalkali compounds.
The beryllium dialkyls have a reactivity which is as great as
that of the corresponding Grignard reagents (4), and the
organocalcium compounds are less reactive (5). The zinc, cad-
mium, and mercury compounds are less reactive than the Grignard
reagent, and of these the mercury compounds are the least
reactive. The volatile zinc compounds are spontaneously in-
flammable in air. They react readily with acids, acid halides,
and alkyl halides, but not with the carbonyl group. The mercury
compounds are relatively stable in air and in the presence of
water, and the splitting with acids is slow enough for the
velocity constants to be determined. The compounds of cadmium
resemble those of zinc more than they do the mercury compounds.

This general decrease in reactivity appears to continue
through the organometallic compounds of the third, fourth, and
fifth groups; however, there is little quantitative informa-
tion on this available at present. The compounds of boron
and aluminum are, in general, less reactive than those of
beryllium and magnesium. The organometallic compounds of tin,
lead, and bismuth are comparatively stable in air and are not
decomposed by water. They are split by acids and halogens.
The trialkyl antimony compounds are unstable in air due to the
formation of the oxide, in which antimony is pentavalent. Like-

(4) Gilman and Schulze, Rec. trav. chim., 48, 1129-1132 (1929).
(5) Gilman and Schulze, J. Am. Chem. Soc., 48, 2463-2467 (1926).

wise the R_3Sb compounds have a tendency to add halogens and acids to form stibonium compounds.

Due to the wide range of reactivity of these compounds it is difficult, if not impossible, to find any one reaction or type of reaction which could be used in a quantitative manner to measure their relative reaction velocities or reactivities.

This paper deals particularly with some of the organo-metallic compounds of lead, tin, mercury, and bismuth.

DISCUSSION OF EXPERIMENTAL METHOD

Splitting reactions with acids, of the type

(a) $R_4M + HX \rightarrow R_3MX + RH$ (with lead and tin compounds),

(b) $R_3M + HX \rightarrow R_2MX + RH$ (with bismuth compounds),

(c) $R_2M + HX \rightarrow RMX + RH$ (with mercury compounds),
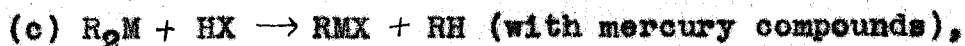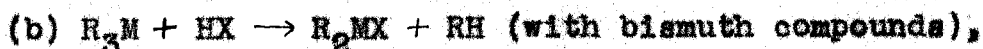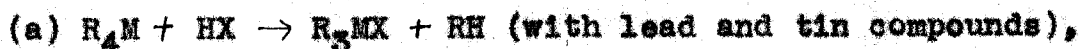
were used since they are the most characteristic and most widely studied reactions of these compounds. In general an excess of the organometallic compound was used, since with an excess of acid the reaction proceeds further:

(d) $R_4M + 2HX \rightarrow R_2MX_2 + 2RH$,
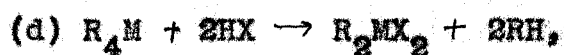
although the second R group is less readily replaced than the first (6) and under favorable conditions reaction (a) proceeds quantitatively, giving a satisfactory second order reaction velocity constant.

The velocity and extent of reaction also change with a change of solvent. In chloroform, reaction (a) can be carried out practically quantitatively, while benzene favors reaction (d).

The rate of splitting of a given organometallic compound varies directly with the strength of the acid. With tetra-phenyl-lead and acetic acid in chloroform the rate of reaction

(6) Flood found this to be true in the case of halogen splitting. See Flood and Horwitz, J. Am. Chem. Soc., 55, 2534-2539 (1933).

was almost zero, even at the boiling point of chloroform. With chloroacetic acid the reaction was somewhat faster. Trichloroacetic acid gives a reaction of the right velocity for convenient measurement at 25°C.

With hydrochloric acid the reaction is almost instantaneous, even at 0°C.

EXPERIMENTAL

The organometallic compounds (except where otherwise indicated) were freshly purified prior to use. Those which were purified by recrystallization were air dried until free of solvent.

In most cases exactly .005 mole of the organometallic compound was weighed out and made up to 250 cc. with pure dry chloroform. Fifty cc. portions of this were placed in glass-stoppered Erlenmeyer flasks and allowed to come to the temperature of the thermostat (30 to 45 minutes usually being required). Five or ten cc. of a chloroform solution of the acid (which was also at the temperature of the thermostat) was added. After the reaction had proceeded the required length of time the flask was removed from the constant temperature bath and extracted twice by shaking in a separatory funnel with 50 cc. portions of cold water. The unreacted acid which was in the water layer was titrated with standard sodium hydroxide and methyl red was used as the indicator.

It was necessary to standardize the acid solutions each time they were used because of the low solubility of hydrogen chloride in chloroform and because of the gradual spontaneous decarboxylation of the trichloroacetic acid in chloroform solution.

The choice of indicator was based on the fact that in some

cases a part of the R_3MX was extracted from the chloroform by the water layer and when phenolphthalein was used the solution became sufficiently alkaline before the end point to give a curdish precipitate:

$$R_3PbX + NaOH \rightarrow R_3PbOH + NaX$$
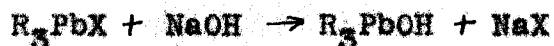
The R_3PbOH is a strong enough base, however, that there is not enough hydrolysis to form a precipitate when methyl red is used as the indicator (7).

In calculating the results a modification of the second order reaction velocity expression was used:

$$R_4M + HX \rightarrow RH + R_3MX$$

$$C_a \qquad C_b \qquad \qquad C$$
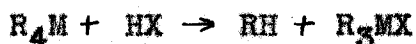
$$k = \frac{1}{t(r-1)b} \log \frac{r-z}{r(1-z)}$$

The factor 2.303 was omitted for convenience since all results are comparative.

t = time in hours;

$$r = \frac{C_a}{C_b} ;$$

b = concentration of HX in moles per liter;

z = fraction of HX reacted in time t.

(7) Calingaert, Chem. Rev., 2, 43-83 (1925), has compared the R_3Pb^+ ions to those of the alkali metals and the R_2Pb^{++} to Zn^{++}. When equivalent amounts of $(C_6H_5)_4Pb$ and HX (or an excess of HX) are used there is some $(C_6H_5)_2PbX_2$ formed which in some cases is extracted by the water and interferes with the titration by liberating HX and forming a cloudy precipitate of $(C_6H_5)_2Pb(OH)_2$.

Effect of Catalysts

About 50 mg. of each of a number of foreign materials was added to the $(C_6H_5)_4Pb$ solution. The following did not appreciably influence the rate of reaction: lead chloride, lead (powdered), ground pyrex, ground quartz, and alcohol. Lead peroxide and diphenyl-lead dichloride appeared to have a slight retarding effect. In the case of the latter this was probably only apparent and due to a hydrolysis with liberation of acid during the water extraction and titration.

Since some of the compounds studied (especially those of tin and mercury) appear to change markedly in reactivity upon standing, it was thought that oxides or peroxides might be formed which would catalyze the reaction. Benzoyl peroxide was apparently without effect on the splitting of tetraphenyltin and diphenylmercury.

Diatomaceous earth had a marked catalytic effect and the inability of the ground quartz and glass to catalyze the reaction was probably due to insufficient surface (8) (9).

(8) Brown and Reid, J. Am. Chem. Soc., 49, 830-839 (1927), have reported that silica gel catalyzes the scission of $(C_2H_5)_4Pb$ with acetic acid.

(9) Gilman and St. John, Rec. trav. chim. 49, 222-224 (1930), report that the addition of silica gel has a slight effect on the reaction between C_6H_5MgBr and C_6H_5CN (1.0 g. decreasing the reaction time of .12 mole C_6H_5CN and .1 mole C_6H_5MgBr from .32 to .25 hours).

$$(C_6H_5)_4Pb + CCl_3CO_2H \rightarrow (C_6H_5)_3Pb\text{-}O\text{-}\underset{O}{C}\text{-}CCl_3 + C_6H_6$$
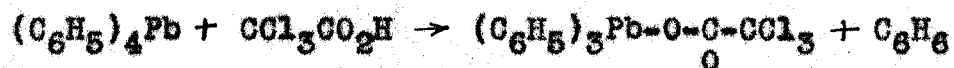
Blank	10 minutes at 25°C.	34.5% reacted
10 mg. diatomaceous earth	" " " "	38.0% "
50 mg. diatomaceous earth	" " " "	51.0% "

$$(C_2H_5)_4Sn + HCl \rightarrow (C_2H_5)_3SnCl + C_2H_6$$
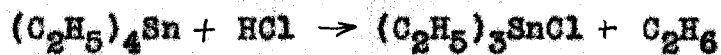
Blank	30 minutes at 40°C.	40.0% reacted
50 mg. diatomaceous earth	" " " "	64.0% "
500 mg. diatomaceous earth	" " " "	reaction complete

$$(C_2H_5)_2Hg + HCl \longrightarrow C_2H_5HgCl + C_2H_6$$
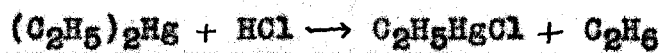
Blank	8 minutes at 0°C.	34.0% reacted
50 mg. diatomaceous earth	" " " "	64.0% "
500 mg. diatomaceous earth	" " " "	95.0% "

Effect of Standing in Air (Oxidation)

A solution of freshly distilled diethylmercury was split with trichloroacetic acid at 10°C. The velocity constant was 47. After standing over night in a cork-stoppered flask the

constants obtained were 74 and 105. These erratic results appeared to be typical of the diethylmercury. The addition of 50 mg. of benzoyl peroxide had no effect on this reaction.

Effect of Light

Diffused sunlight was found to have no effect on reaction (a). Flood and Horwitz (6) do not mention any effect of light on their halogenation reactions. Smith and Kipping (10) report that the reaction $2(CH_2C_6H_5)_3SnCl + 2I_2 \rightarrow (CH_2C_6H_5)_2SnCl_2 + (CH_2C_6H_5)_2SnI_2 + 2C_6H_5CH_2I$ is materially aided by direct sunlight.

Since most halogenation reactions are quite sensitive to even diffused sunlight it was deemed desirable to check this point. A chloroform solution of iodine, .0005 mole, was added to .001 mole of triphenyltin chloride in 50 cc. of chloroform at room temperature. Duplicate reactions were run, one in a pyrex flask and one in an opaque bottle. They were set in a window where the direct sunlight could strike the solution in the pyrex flask about one-third of the time. At the end of an hour the unreacted iodine was titrated with standard sodium thiosulfate. In both cases 33 per cent of the iodine had reacted. Apparently even direct sunlight has little, if any, effect on this reaction.

(10) Smith and Kipping, J. Chem. Soc., 101, 2553-2563 (1912).

Table I

Scission of Tetraphenyl-lead

(.0005 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temperature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
CH$_3$COOH	.000306	C$_6$H$_6$ 55 cc.	70	60	0	
"	"	"	"	120	1.95	
ClCH$_2$COOH	.000345	"	"	75	25.5[a]	
HCl	.000590	CHCl$_3$ 55 cc.	25	1/2	94.0	
"	.000168	"	0	"	62.0	
Cl$_3$CCO$_2$H	.000170	"	25	10	17.9	58.8
"	"	"	"	20	28.3	50.3
"	"	"	"	30	39.6	52.5
"	"	"	"	45	52.6	53.6
"	.000212	"	"	10	16.4	59.5
"	"	"	"	20	31.3	57.3
"	"	"	"	40	49.2	55.6
"	"	"	"	80	73.8	59.5
"	.000500	CHCl$_3$ 63.9 cc.	"	20	29.0	68.0
"	"	"	"	40	46.5	72.0
"	"	"	"	60	59.0	80.0

(a) Turbidity in titration.

Table II

Scission of Tetraethyl-lead

(.001 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temper-ature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
Cl_3CCO_2H	.000324	$CHCl_3$ 55 cc.	25	11	5.0	6.6
"	"	"	"	25	10.0	6.3
"	"	"	"	60	19.4	5.2
"	"	"	"	110	33.0	5.4
"	"	"	"	150	40.0	5.2
"	"	"	"	180	47.8	5.6
"	.000 283	"	40	10	20.7	33.0
"	"	"	"	20	34.8	32.0
"	"	"	"	30	48.0	34.0
"	"	"	"	40	58.0	34.0
"	"	"	"	50	65.0	34.0
HCl	.000500	$CHCl_3$ 60 cc.	25	1/2	54.0	2990.0
"	"	"	"	1	77.4	3000.0
"	"	"	"	1	76.0	2960.0
"	"	"	"	5	96.6	2540.0

Table II (Cont.)

Acid	Moles of Acid	Solvent and Total Volume	Temper-ature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
HCl	.000500	CHCl3 60 cc.	10	1	32.0	666.0(a)
"	"	"	"	2	49.0	612.0(a)
"	"	"	"	5	76.0	593.0(a)
"	"	"	"	5	73.4	1028.0
"	"	"	"	5	73.0	1020.0
"	"	"	"	4	85.0	(b)
"	.000320	CHCl3 55 cc.	"	1	9.5	(c)
"	"	"	"	8	61.0	(c)
"	"	"	"	16	55.0	(c)
"	"	"	"	1	12.5	112.0(d)
"	"	"	"	5	24.0	123.0(d)
"	"	"	"	7	46.5	127.0(d)
"	"	"	"	11	61.0	80.0(d)

(a) Carbon dioxide was passed through the chloroform before dissolving the tetraethyl-lead.

(b) The tetraethyl-lead was redistilled.

(c) The reaction took place in a carbon dioxide atmosphere. The end point was indistinct.

(d) The tetraethyl-lead stood in an ice box 14 days in a dark bottle after distillation.

Table III

Scission of Tetraphenyltin

(.001 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temperature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
Cl_3CCO_2H	.000270	CHCl$_3$ 55 cc.	40	60	3.0	
"	"	"	"	240	9.0	
"	"	"	"	360	22.0[a]	
HCl	.000312	CHCl$_3$ 60 cc.	10	3	40.5	290.[b]
"	"	"	"	5	54.0	265.[b]
"	"	"	"	7	66.3	278.[b]
"	.000375	CHCl$_3$ 55 cc.	0	60	20.7	7.3
"	"	"	"	180	50.5	8.2
"	.000274	"	"	60	27.6	8.3
"	"	"	"	120	42.0	7.2
"	.000370	"	10	5	18.3	59.5[c]
"	"	"	"	10	45.8	47.5[c]
"	.000332	"	"	5	33.0	122.[c]
"	"	"	"	10	52.0	52.0	117.[c]

(a) The end point was indistinct.
(b) The tetraphenyltin solution stood 24 hours before using.
(c) The tetraphenyltin was freshly crystallized from chloroform.

Table III (Cont.)

Acid	Moles of Acid	Solvent and Total Volume	Temperature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
HCl	.000332	CHCl₃ 55 cc.	10	15	60.0	99. (c)
"	"	"	"	20	71.6	105. (c)
"	.000320	"	"	5	23.3	74. (d)
"	"	"	"	15	52.0	77. (d)
"	"	"	"	5	27.0	95. (e)
"	"	"	"	15	56.5	89. (e)
"	"	"	"	10	71.0	208. (f)
"	"	"	"	5	72.0	425. (g)

(d) The tetraphenyltin crystals were dried 1/2 hour in air.
(e) "   "   "   "   "   "   2 hours   "   "   .
(f) "   "   "   "   "   "   16 hours   "   "   .
(g) "   "   "   "   "   "   4 days   "   "   .

Table IV

Scission of Tetraethyltin

(.001 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temper- ature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
HCl	.000382	CHCl₃ 60 cc.	25	75	28.3	7.3
"	"	"	"	170	49.3	7.0
"	"	"	"	240	59.0	6.7
"	.000352	"	"	75	26.0	6.7
"	"	"	"	90	31.0	7.0
"	.000334	"	40	31	41.5	29.1
"	"	"	"	45	51.7	28.0
"	"	"	"	60	61.4	28.1

Table V

Scission of Triphenylbismuth

(.001 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temperature ^{o}C.	Time in Minutes	Per cent Reacted	Velocity Constant
Cl_3CCO_2H	.000274	$CHCl_3$ 60 cc.	25	30	52.0	42. [a]
"	"	"	"	40	57.0	36. [a]
"	.000368	$CHCl_3$ 55 cc.	"	15	38.5	50. [b]
"	"	"	"	30	53.0	41. [b]
"	"	"	"	45	Ppt. formed	
"	.000360	"	"	15	30.0	36.5 [c]
"	"	"	"	45	50.0	37. [c]
"	.000358	"	40	10	43.6	90.
"	"	"	"	3	15.0	78.
"	"	"	"	15	53.0	81.

(a) The triphenylbismuth was freshly crystallized.
(b) The triphenylbismuth crystals stood for 48 hours in an ice box.
(c) The triphenylbismuth solution stood over night in the ice box.

Table VI

Scission of Diphenylmercury

(.001 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temper- ature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
Cl_3CCO_2H	.000475	CHCl₃ 55 cc.	25	10	32.8	62.8
"	"	"	"	20	52.0	60.2
"	"	"	"	30	60.2	52.0
"	"	"	"	40	69.0	51.5
"	"	"	40	2	29.8	275.
"	"	"	"	5	51.4	230.
"	"	"	"	8	63.0	214.
"	.000343	"	25	10	54.0	124. [a]
"	"	"	"	20	66.6	93.0 [a]

(a) The diphenylmercury was freshly crystallized.

Table VII

Scission of Diethylmercury

(.001 mole per run)

Void	Moles of Void	Solvent and Total	Temperature in °C	Time Minutes	Per cent Reacted	Velocity Constant	
HCl	.000312	60 cc. CHCl₃	10	1	25.4	480.	(a)
"	"	"	"	2	37.8	402.	(a)
"	"	"	"	4	58.2	382.	(a)
"	"	"	"	6	69.0	263.	(a)
"	.000396	55 cc. CHCl₃	"	4	39.4	196.	(b)
"	"	"	"	9	50.0	188.	(b)
"	"	"	"	10	68.0	195.	(b)
"	"	"	0	8	33.9	80.5	(b)
"	"	"	"	12	48.0	86.	(b)
"	"	"	"	17	61.5	91.	(b)
"	"	"	"	21	66.5	88.	(b)
"	.000443	60 cc. CHCl₃	10	15	34.0	47.	(c)
"	.000412	55 cc. CHCl₃	"	16	57.0	108.	(c)(d)
"	"	"	"	20	81.0	74.	(d)

(a) The diethylmercury was used as received from the Eastman Kodak Company.

(b) The diethylmercury was distilled in an inert atmosphere.

(c) The diethylmercury was distilled under reduced pressure in an inert atmosphere.

(d) The solution of diethylmercury, prepared as in (c), stood over night.

Table VII (Cont.)

Acid	Moles of Acid	Solvent and Total Volume	Temperature in °C.	Time in Minutes	Per cent Reacted	Velocity Constant
Cl₃COO₂H	.000383	55 cc. CHCl₃	40	75	14.4	2.4
"	"	"	"	150	26.9	3.0
"	"	"	"	166	28.4	3.06
HCl	.000545	60 cc. CHCl₃	10	2	8.0	67.2(e)
"	"	"	"	4	16.0	69.8(e)
"	"	"	"	23	54.0	63.6(e)
"	"	"	0	10	7.0	11.8(e)
"	"	"	"	30	19.3	11.9(e)
"	"	"	"	164	53.0	8.4(e)
"	"	.000545	"	30	9.2	4.7(r)
"	"	"	"	60	18.7	5.3(r)
"	"	"	10	6	14.7	29.2(r)
"	"	"	"	23	33.2	30.0(r)

(e) The diethylmercury was distilled under reduced pressure in a carbon dioxide atmosphere.

(r) This diethylmercury was the same as that used in (e) except that it was given one additional purification.

Table VIII

Scission of Ethyltriphenyl-lead

(.001 mole per run)

Acid	Moles of Acid	Solvent and Total Volume	Temperature °C.	Time in Minutes	Per cent Reacted	Velocity Constant
Cl_3CCO_2H	.000301	CHCl$_3$ 55 cc.	25	1	70	1,980
"	"	"	"	1/2	46	1,930
"	"	"	"	1	68	1,880
"	.000294	"	"	1	76	2,360[a]
"	"	"	"	1/2	53	2,370[a]
"	.000357	"	"	1	44	[b]
"	"	"	"	1	42	855[b]
"	"	"	"	1	42	855[c]
"	"	"	"	1	86	3,580[d]
"	"	"	"	1/2	63	3,320[d]

(a) The ethyltriphenyl-lead was recrystallized.
(b) The ethyltriphenyl-lead was recrystallized and dried 45 minutes in a current of nitrogen.
(c) Oxygen was bubbled through the ethyltriphenyl-lead solution 1 minute, and it was allowed to stand 1 hour before the addition of acid.
(d) The compound used in (b) was allowed to stand in air 1 1/2 hours before being used.

Compounds

Tetraphenyl-lead   (Table I)

The tetraphenyl-lead (m.p. 226°) was prepared by the method of Gilman and Robinson (11). Runs were made on four different batches (12). There was usually a satisfactory agreement in results when an excess of the tetraphenyl-lead was used and when the lead compound was from twenty-four hours to six weeks old. The freshly crystallized compound was somewhat less active.

Tetraethyl-lead   (Table II)

The tetraethyl-lead was obtained from the Ethyl Gasoline Corporation. It was purified by shaking with cold 20 per cent sulfuric acid, washed with water and sodium carbonate solution, dried over calcium chloride and distilled under reduced pressure (b.p. 82° at 13 mm.) in an inert atmosphere.

Good check results were obtained by scission with trichloroacetic acid, but with hydrochloric acid the reaction appeared more erratic. The reactivity changed markedly on standing. The reaction was probably affected by oxidation and decomposition products.

(11) Gilman and Robinson, J. Am. Chem. Soc., 49, 2315-2317
      (1927).
(12) The author is indebted to E. B. Towne and P. T. Parker
      for a part of this compound.

Tetraphenyltin (Table III)

The tetraphenyltin was obtained from the Eastman Kodak Company. It was purified by repeated crystallization from chloroform. The melting point of the product used was 227-228°. The reactivity of this material changed markedly on standing although there was no appreciable change in melting point or in weight after standing 24 hours. A 3.7-gram sample gained only 1 milligram in weight after standing in air a week.

The reaction with trichloroacetic acid was extremely slow.

Tetraethyltin (13) (Table IV)

The tetraethyltin was cooled in a freezing mixture, decanted from any crystalline material which separated, washed with cold 20 per cent sulfuric acid and with water, dried over potassium carbonate and calcium chloride, and distilled under reduced pressure in a carbon dioxide atmosphere. The boiling point was 89° at 40 mm. and 103° at 70 mm. This material was halogen-free.

Satisfactory velocity constants were obtained at 25 and 40° with hydrogen chloride. The reaction with trichloracetic acid was negligible under these conditions.

(13) The author is indebted to Wm. Wall for the preparation
     of this compound.

Triphenylbismuth (Table V)

The triphenylbismuth was obtained from the Eastman Kodak Company. It was recrystallized from a mixture of equal parts of petroleum ether and absolute alcohol. The melting point was 78°.

This compound did not change appreciably in reactivity upon standing. Satisfactory constants were obtained by scission with trichloroacetic acid, but results of 216 and 340 at 10° were obtained with hydrogen chloride.

Diphenylmercury (14) (Table VI)

The diphenylmercury melted at 121.5°.

Diethylmercury (Table VII)

The diethylmercury was obtained from the Eastman Kodak Company.

Both the diethyl and the diphenylmercury gave quite erratic results. The reactivity changed rapidly on standing and varied with the method of purification.

Ethyltriphenyl-lead (Table VIII)

Triphenyl-lead chloride (m.p. 206-208°) was prepared by

(14) The author is indebted to K. E. Marple for the preparation of the diphenylmercury.

the method of Gilman and Robinson (15). The triphenyl-lead chloride was refluxed 2 1/2 hours with 2 mole equivalents of ethylmagnesium bromide. The ether solution was hydrolyzed with ice and ammonium chloride and dried over calcium chloride in the refrigerator. The cold solution was filtered to remove some unreacted triphenyl-lead chloride. The ether was removed under reduced pressure and the product recrystallized from alcohol. The yield was 87 per cent. The melting point of the crude material was 45-46°, and of the pure material 44-45°.

As can be seen from Table VIII, the ethyltriphenyl-lead increased in activity upon standing in air.

(15) Gilman and Robinson, J. Am. Chem. Soc., 51, 3112-3114 (1929).

Table IX

Summary of Results

Scission of organometallic compounds with acid in chloroform solution

Organometallic Compounds	HCl				Cl$_3$CCO$_2$H			
	0°	10°	25°	40°	0°	10°	25°	40°
$(C_2H_5)_4Pb$		410					6	33
$(C_6H_5)_4Pb$ (a)							56	307
$(C_2H_5)_4Sn$ (b)			6.9	28.4				
$(C_6H_5)_4Sn$	8	75						
$(C_2H_5)_2Hg$	5	30						3
$(C_6H_5)_2Hg$							57	240
$(C_6H_5)_3Bi$							40	83
$(C_6H_5)_3C_2H_5Pb$						2000		

(a) The tetraphenyl-lead was too reactive for satisfactory measurement with HCl at 0°.
(b) The tetraethyltin was too inert for satisfactory measurement at 40°.

DISCUSSION OF RESULTS

The sensitiveness of the scission reactions to catalyses of various kinds makes these reactions difficult to study in a quantitative manner. Several purifications were generally required before constant activity was obtained; and then the activity often changed rapidly upon aging. The results, in general, appear to be of a sufficient degree of accuracy, however, to warrant at least a semiquantitative evaluation of their relative reactivity.

On the basis of these studies the organometallic compounds of these metals would fall in the following order:

>Lead   Most reactive
>
>Mercury
>
>Bismuth
>
>Tin   Least reactive

This series is based on the data contained in Table IX, which is a summary of the experimental results contained in Tables I to VIII.

Both the ethyl and phenyl derivatives of lead, tin, and mercury were studied. In every case the aryl derivative gave a higher reaction velocity than the alkyl. This is in agreement with the qualitative studies of Kharasch (16) and of

(16) Kharasch and Flenner, J. Am. Chem. Soc., 54, 674-692 (1932).

Gilman and Towne (17). These authors studied the mixed organometallic compounds of mercury and lead, respectively. In such cases it was found that the more aromatic (or more negative) radical was preferentially removed. This is probably a case of comparative reaction velocities.

(e) $R-Pb-R' + HX \rightarrow R_3PbX + R'H$

(f) $R-Pb-R' + HX \rightarrow R\ R'PbX + RH$

Where R' is more negative (or more aromatic) than R, reaction (e) would have a higher velocity then reaction (f).

Calingaert (7) states that the mixed compounds exhibit a lower stability and greater reactivity and solubility than their homogenous progenitors. He attributes this to loss in symmetry. Thermal data are cited. Our chemical data substantiate Calingaert's theory. From Table IX it can be seen that ethyltriphenyl-lead is of a higher order of reactivity than either tetraethyl or tetraphenyl-lead. One who is unfamiliar with the behavior of these compounds would expect it to fall between the latter two.

The ethyl derivatives tend to decompose on standing more than the phenyl derivatives. This is probably due to the fact that the former are liquids and the latter solids. It is possible, however, that if an altogether different type of

(17) Gilman and Towne, Rec. trav. chim., 51, 1054-1064 (1932).

reaction (such as oxidation, replacement of metal, or thermal decomposition) were chosen as a basis of comparison, the above elements would not always fall in the same order.

It is likewise possible (and also probable) that the "negativity series" of Kharasch could not be applied so widely. The benzyl is one of the most positive radicals in his series, yet tetrabenzyltin (18) and tetrabenzyl-lead (19) are apparently more sensitive to oxidation than the tetraphenyl derivatives. Tetraphenyltin and tetraphenyl-lead can be kept months at a time without an appreciable change in melting point. The mixed benzyltin compounds give anomalous results on halogen splitting (20)(18).

The author has not been able to correlate the reactivity of the organometallic compound with the position of the metal in the E.M.F. series. The relationship between reactivity and position in the periodic table seems to be more direct. On this basis it does not seem unreasonable to predict that the organogermanium compounds would be less reactive than the organotin compounds.

(18) Smith and Kipping, J. Chem. Soc., 101, 2553-2563 (1912).
(19) Krause and Schlöttig, Ber., 63, 1381-1387 (1930).
(20) Krause and Bullard, J. Am. Chem. Soc., 48, 2131-2136 (1926).

SUMMARY

1. A quantitative method has been developed for studying the comparative reactivity of some organometallic compounds of some of the elements in the second, third, fourth and fifth groups.

2. The relative reactivities of the ethyl and phenyl derivatives of lead, mercury, and tin, and the phenyl derivative of bismuth have been determined by a study of the reaction velocities with trichloroacetic acid and with hydrogen chloride in chloroform.

3. The rate of scission of these organometallic compounds with acid is proportional to the strength of the acid.