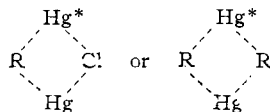that electron-withdrawing groups impede the reaction. He pictures a transition state

In any case, it is obvious that *simple* SE2 mechanism is not at work here, and that electrophilic substitution at a carbon center deserves further consideration. Work in the Cd, Sn and Pb systems is now underway.

Acknowledgment.—The authors wish to thank the National Science Foundation for a grant which supported the majority of this work (NSF G-5911), and to acknowledge the aid of Dr. George F Wright in obtaining the dipole moment and polarizability data.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

The Cleavage of Carbon–Metal Bonds

BY RAYMOND E. DESSY AND JIN-YOUNG KIM[1]
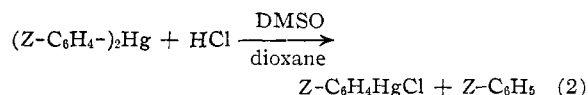
RECEIVED APRIL 30, 1960

Be means of an intensive investigation of the reaction $R_mMR' + HX \xrightarrow{\text{solvent}} R_mMX + R'H$ data concerning: (1) the ability of a triple bond to conduct electrical effects to a reaction site, (2) the relative stability of C–M bonds as a function of hydridization of the carbon atom, (3) the relative stability of C–M bonds as a function of M, (4) the effect of solvent upon cleavage reactions, and (5) the reactivity of unsymmetrical organometals have been obtained. Suggestions concerning linear relationships observed between $E^{\neq}$ and $\Delta S^{\neq}$, log k_2 and H, and H and log (HX) are presented.

During the past few years an intensive study of the cleavage of carbon–metal bonds in the organometallic compounds of divalent metals with acids

$$R_2M + HX \longrightarrow RH + RMX \qquad (1)$$

has been undertaken.[2]

In the series R = phenyl, M = Hg and X = chlorine

$$(Z\text{-}C_6H_4\text{-})_2Hg + HCl \xrightarrow[\text{dioxane}]{\text{DMSO}}$$
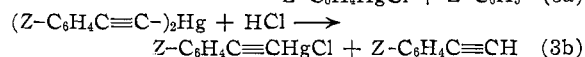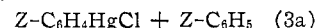$$Z\text{-}C_6H_4HgCl + Z\text{-}C_6H_5 \qquad (2)$$

where Z is a *meta* or *para* substituent, the following facts have been observed: (a) the reaction involves electrophilic attack by molecular or ion pair HCl on the C–Hg linkage with the Hammett $\rho = -2.8$, (b) $E^{\neq}$ is a linear function of $\Delta S^{\neq}$.[2d]

Considerable effort has also been expended in the past in order to determine the ability of a —C≡C— linkage to transmit electrical effects to a reaction site,[3] as well as to determine the relative stabilities of C–M linkages toward cleavage as a function of M, the solvent used and the cleaving acid,[2,4] but little comparable data has been accumulated—most workers using such different systems that no direct comparisons of the separate data may be made.

It is the purpose of this paper: (1) to discuss the effect of inserting a —C≡C— linkage between an alkyl or aryl group and a metal (R—M— to R—C≡C—M—) on the rate of reaction with

HCl; (2) to present some data on the cleavage of

$$(Z\text{-}C_6H_5\text{-})_2Hg + HCl \longrightarrow$$
$$Z\text{-}C_6H_4HgCl + Z\text{-}C_6H_5 \quad (3a)$$
$$(Z\text{-}C_6H_4C\equiv C\text{-})_2Hg + HCl \longrightarrow$$
$$Z\text{-}C_6H_4C\equiv CHgCl + Z\text{-}C_6H_4C\equiv CH \quad (3b)$$

unsymmetrical compounds; (3) to present data indicating the effect of changing M (reaction 2) from Hg to Pb, Sn and Cd; and (4) to indicate the function of solvent in these reactions. This leads to some conclusions concerning linear relationships between the acidity functions, H, of the acid–solvent systems, and log k_2, the rate of C–Hg cleavage by these systems; and between H and log(HX). A linear relationship between $E^{\neq}$ and $\Delta S^{\neq}$ has been noted for the M = Hg system, spanning some 75 activation entropy units, and 25 kcal. of activation energy.

Experimental

Organomercury Compounds.—The substituted bis-phenylacetylenylmercury compounds were prepared according to the method of Johnson and McEwen,[5] in which two equivalents of alkaline mercuric iodide were treated with one equivalent of the acetylenes in 95% ethanol. The crude products were washed with 50% ethanol, and crystallized once from 95% ethanol. They were dissolved in a small amount of benzene and precipitated out by the addition of petroleum ether. Identification data follow.

Phenylethylmercury was prepared as previously described,[8] and bis-o-phenylenedimercury was donated by the Orgmet Co., Wenham, Mass.

Diethylcadmium.—Diethylcadmium was prepared by the usual Grignard method.[9] Ethylmagnesium bromide was allowed to react with dry $CdBr_2$ in ether, and the ether was partially replaced by benzene. Final distillation of the diethylcadmium was done in a nitrogen atmosphere; b.p. 48° (11 mm.).

Tetraphenyltin, Metal and Thermit Corp., Rahway, N. J.; tetravinyltin, Metal and Thermit Corp., Rahway, N. J.; tetraphenyllead, Ethyl Corp., N. Y. 17, N. Y.

(1) National Science Foundation Pre-doctoral Research Fellow.

(2) *Cf.* (a) S. Winstein, T. G. Traylor and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955); (b) S. Winstein and T. G. Traylor, *ibid.*, **77**, 3747 (1955); **78**, 2597 (1956); (c) R. E. Dessy, G. F. Reynolds and Jin-Young Kim, *ibid.*, **81**, 2683 (1959); (d) R. E. Dessy and Jin-Young Kim, *ibid.*, **82**, 686 (1960), for leading references.

(3) *Cf.* (a) J. H. Kochi and G. S. Hammond, *ibid.*, **75**, 3452 (1953); (b) M. S. Newman and S. H. Merrill, *ibid.*, **77**, 5552 (1955); (c) R. E. Dessy, J. H. Wotiz and C. A. Hollingsworth, *ibid.*, **79**, 358 (1957); (d) J. D. Roberts and R. Carboni, *ibid.*, **77**, 5554 (1955).

(4) *Cf.* (a) H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943; (b) A. H. Corwin and M. A. Naylor, Jr., *J. Am. Chem. Soc.*, **69**, 1004 (1947).

(5) J. R. Johnson and W. L. McEwen, *ibid.*, **48**, 468 (1926).

(6) T. H. Vaughn and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 1207 (1934).

(7) T. H. Vaughn, *ibid.*, **55**, 3453 (1933).

(8) R. E. Dessy, Y. K. Lee and Jin-Young Kim, *ibid.*, **83**, 1163 (1961).

(9) E. Krause, *Ber.*, **50**, 1813 (1917).

(Z—C₆H₄C≡C—)₂Hg

Z-	M.p., °C. Found	M.p., °C. Lit.	Carbon,% Found	Carbon,% Calcd.	Hydrogen % Found	Hydrogen % Calcd.
H	126–127	124.5–125⁵	...	...	..	..
4-F-	183–184	....	44.04	43.80	2.56	1.83
4-Cl-	203–206	221.5–222⁶	40.31	40.75	2.02	1.71
3-Cl-	136–137.5	138–138.5⁶	...	...	..	..
3-Me-	53–56	....	49.88	50.17	3.16	3.27
2,4-DiMe	143–144.5	140.3–140.5⁷	...	...	..	..
2,6-DiMe-4-(t-Bu)-	238–239	....	58.84	58.88	5.50	6.00
(C₄H₉C≡C)₂Hg	97.5–98.5	96.2–96.4⁷	...	...	..	..

The solvents employed were purified as follows: dimethyl-sulfoxide, Stepan Chemical Co., Chicago 6, Ill., vacuum distilled at 47° (3 mm.); dimethyl sulfone, Crown Zeller-bach Chemical Products Division, Camas, Wash., recrystallized from H₂O, and dried over P₂O₅; dimethylformamide, purified by passing through 4-X Molecular Sieve, Linde Co., and then distilled, b.p. 152–154° (736 mm.); benzene, spectral grade distilled from lithium aluminum hydride; dioxane, spectral grade; methanol, spectral grade purified by passing through 4-X Molecular Sieve and then distilled, b.p. 65°; acetic acid, refluxed with potassium permanganate,

the acetylenic series. The following conclusions can be drawn from a comparison of the data:

a. The Hammett plot for the phenylacetylenyl compounds requires the use of $(\sigma + \sigma^+)/2$, rather than σ or σ^+ alone, similar to the results found in the phenyl series.[2d]

b. The Hammett plot for the phenylacetylenyl compounds ($\rho = -1.0$) indicates that attack is electrophilic in nature but that the reaction is far
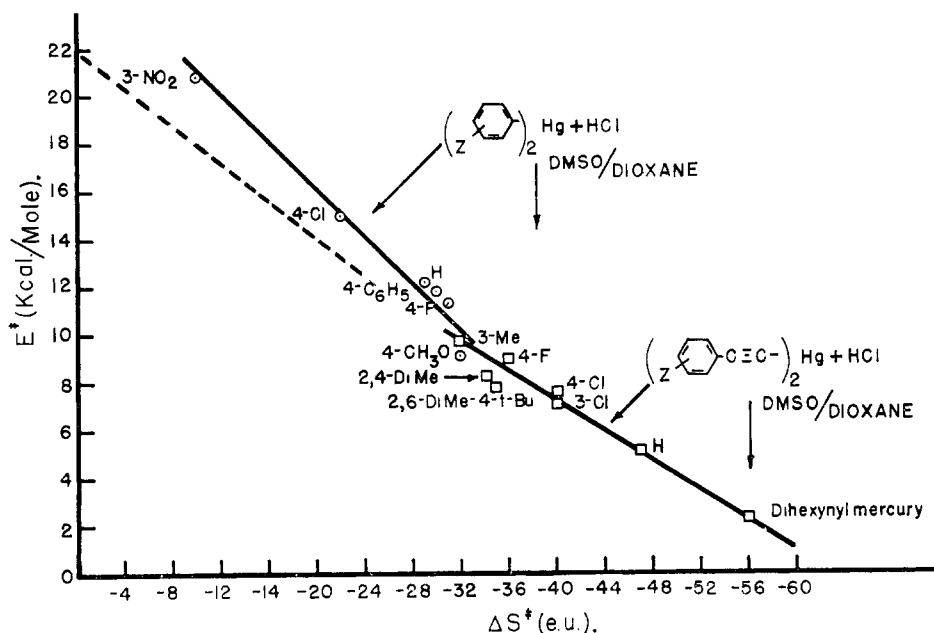

Fig. 1.

and distilled, b.p. 115–118°. The middle cut was dried with MgClO₄ and P₂O₅ and redistilled, b.p. 118°.

Kinetic Runs.—The kinetic measurements were made as previously described.[2c] All products were identified by m.p., mixed m.p., infrared spectra and C, H analysis.

Results and Discussions

Symmetrically Substituted Phenylmercury Compounds.—The cleavage of a series of symmetrically substituted bis-phenylacetylenylmercury compounds with hydrogen chloride (eq. 3b) in dimethyl sulfoxide (DMSO)–dioxane (10:1) has been studied, and the results are shown in Table I. A plot of $E^\ddagger$ vs. $\Delta S^\ddagger$ for these compounds, as well as for dihexynylmercury, is shown in Fig. 1. A companion plot showing $E^\ddagger$ vs. $\Delta S^\ddagger$ values for the cleavage of a series of symmetrical m- and p-substituted bis-phenylmercury compounds with hydrogen chloride (eq. 3a) under similar circumstances s also shown. Figure 2 shows Hammett plots for

less sensitive to substituents on the ring than the phenyl series of compounds ($\rho_0 = 2.8$). The ratio

TABLE I

$(Z—\!\!\!\bigcirc\!\!\!—C\equiv C—)_2Hg + HCl \xrightarrow{\text{DMSO} \over \text{dioxane}}$

$Z—\!\!\!\bigcirc\!\!\!—C\equiv CHgCl + Z—\!\!\!\bigcirc\!\!\!—C\equiv CH$

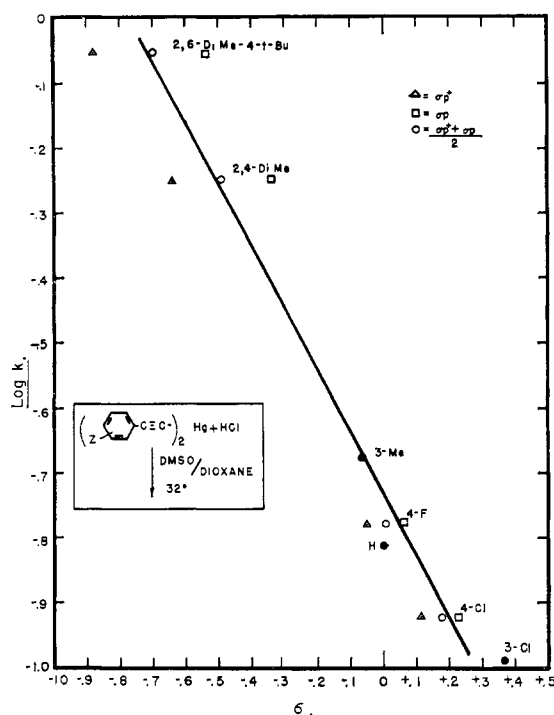| z	19	k_2,t liters/mole-sec. 25	32	40
H	0.106	0.125	0.155	...
3-Cl	...	.079	.103	0.142
4-Cl	...	.089	.120	...
4-F	0.094	.117	.166	...
3-Me	.097	.140	.205	...
2,4-DiMe	.314	.425	.581	...
2,6-DiMe-4-t-Bu	.486	.640	...	...
Dihexynylmercury	.192	.209	.234	...
Bis-(2-naphthyl)-mercury		.013	.023	.043

Fig. 2.

of $\rho/\rho_0 = 0.35$. This should be compared with the similar values found by other workers who have investigated the ability of a triple bond to conduct electrical effects, as shown in Table II. One can conclude that a triple bond more closely resembles a $-CH_2-CH_2-$ unit as far as its insulating properties are concerned. The anomalously high value for the hydrolysis of the propiolic esters should be viewed with caution since field effects seem important in this reaction.[2b,d]

c. There appears to be no *ortho*-effect in the reaction studied, since the 2,4-dimethyl and 2,6-dimethyl compounds fall on the Hammett plot using σ_p values. Models indicate that steric hindrance should not be a factor in these reactions since the reaction site is sufficiently removed from the *o*-position.

d. There is a linear relationship between $E^{\ddagger}$ and $\Delta S^{\ddagger}$, similar to that observed in the phenyl series. The isokinetic temperature[10] for the phenylacetylenyl series is 300 °K., compared to the 500 °K. for the phenyl series. This explains to a large extent the poor Hammett fit.

e. The activation energies for cleavages in the phenylacetylenyl series are some 3–7 kcal./mole less then in the phenyl series, while entropy terms are some 15–20 e.u. lower. It would appear that changing the attacked carbon atom from sp^3 to sp^2 to sp involves a decrease in both activation energy and entropy, as is shown in Table III. The decrease in the entropy of activation does not fully compensate for the fall in activation energy and the ease of cleavage of the C–M bond increases as more s character is associated with the attacked carbon, as is to be expected in electrophilic attack.[2c] It is interesting to note that in the Sn system the preferential cleavage sequence is $C_6H_5-> CH_2{=}CH-$

(10) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

Table II

Reaction	R	ρ/ρ_0
$(ZC_6H_4R-)_2Hg$		1.00^a
$+ HCl \xrightarrow[\text{dioxane}]{\text{DMSO}}$	$-C{\equiv}C-$	0.35^b
$ZC_6H_4RC\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}} \;\overset{\longleftarrow}{\underset{\longrightarrow}{}}\; H_2O$	....	1.00^c
$ZC_6H_4RC\overset{\displaystyle O}{\underset{\displaystyle O}{\diagdown}} \;\ominus$	$-CH_2-$ $-CH_2CH_2-$ $-CH{=}CH-$ $-C{\equiv}C-$	0.49^c $.21^c$ $.46^c$ $.25^c$
$ZC_6H_4RC\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}} \; +$	.... $-C{\equiv}C-$	1.0^c 0.33^d
$(C_6H_5)_2CN_2 \xrightarrow{\text{EtOH}}$		
$ZC_6H_4RC\overset{\displaystyle O}{\underset{\displaystyle OC_2H_5}{\diagdown}} \xrightarrow[\text{H}_2\text{O, OH}]{\text{EtOH}}$	.... $-CH_2-$	1.00^c 0.34^c
$ZC_6H_4RC\overset{\displaystyle O}{\underset{\displaystyle O}{\diagdown}} \; \ominus$	$-CH_2CH_2-$ $-CH{=}CH-$ $-C{\equiv}C-$	0.20^c $.54^c$ $.79^d$

^{a} R. E. Dessy and Jin-Young Kim, *J. Am. Chem. Soc.*, **82**, 686 (1960). ^{b} Present work. ^{c} H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953). ^{d} J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955). ^{e} M. S. Newman and S. H. Merrill, *ibid.*, **77**, 5552 (1955).

Table III

$$R_2Hg + HCl \xrightarrow[\text{dioxane}]{\text{DMSO}} R\text{-Hg-Cl} + R\text{-H}$$
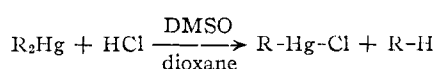
R	$k_1^{25} \times 10^3,$ l./mole-sec.	$E^{\ddagger},$ kcal./mole	$\Delta S^{\ddagger},$ e.u.
$n\text{-}C_3H_7-^a$	0.051	16.5	-24
$H_2C{=}CH-^a$	14	13.6	-23
$C_6H_5-^a$	9.3	12.2	-29
$C_6H_5C{\equiv}C-^b$	125	5.3	-46
$C_4H_9C{\equiv}C-^b$	209	2.4	-56

^{a} R. E. Dessy, G. F. Reynolds and Jin-Young Kim, *J. Am. Chem. Soc.*, **81**, 2683 (1959). ^{b} Present work.

$>$ alkyl.[11] Unfortunately, no rate data are available.

f. No distinct correlation between σ and the position on the $E^{\ddagger}$, $\Delta S^{\ddagger}$ curve is noted for the phenylacetylenyl compounds, in comparison to the ordered nature observed in the phenyl series, an ordering apparently due to specific solvation effects.

g. The position of dihexynylmercury on the $E^{\ddagger}$, $\Delta S^{\ddagger}$ curve indicates that it should be possible to develop σ-values for aliphatic substituents in this manner avoiding the assumptions made by Taft for his σ^*-values.[12]

(11) (a) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957); (b) J. G. A. Luyten and G. J. M. Van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, 1955.
(12) *Cf.* M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.
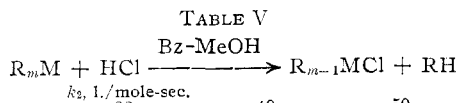
TABLE IV

$$\text{R-Hg-R'} + \text{HCl} \xrightarrow[\text{dioxane}]{\text{DMSO}} \text{R-Hg-Cl} + \text{R'-H}$$
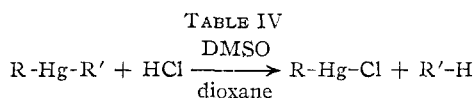
R =	R' =	$k_2{}^{25}$	$E\ddagger$	$\Delta S\ddagger$
C₆H₅–	C₆H₅–	0.0093	12.2	−29
C₂H₅–	C₂H₅–	.00008	15.5	−27
C₆H₅–	C₂H₅–	.045	11.9	−27

k^{I} .315ᵃ	11.3	−25
k^{II} .048ᵃ	11.3	−29

ᵃ Obtained by the method of A. Frost and W. Schwemer, *J. Am. Chem. Soc.*, **74**, 1268 (1952).

TABLE V

$$\text{R}_m\text{M} + \text{HCl} \xrightarrow{\text{Bz-MeOH}} \text{R}_{m-1}\text{MCl} + \text{RH}$$

			k_2, l./mole-sec.			Reactivity ratio	$E\ddagger$, kcal./mole	$\Delta S\ddagger$, e.u.
RmM	19	25	32	40	50			
(C₆H₅)₂Hg	0.22	0.35	0.56	..	...	150	12.8	−20
(C₆H₅)₄Pb	..	0.13	.23	0.43	...	60	15.0	−14
(C₆H₅)₄Sn	..	..	.0038	0.012	0.040	1	25.8	−13

Unsymmetrical Organomercury Compounds.—

In 1932, Kharasch published the results of an intensive investigation of the reaction.[13]

$$\text{R-Hg-R'} + \text{HCl} \longrightarrow \text{R-Hg-Cl} + \text{R'-H} \qquad (4)$$
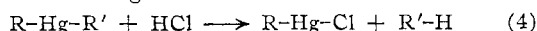
From it he established a series of electronegativity values for alkyl and substituted aryl groups. Unfortunately no information concerning the rates of cleavage of symmetrical *versus* unsymmetrical compounds was provided. Table IV shows the results of cleavage of two unsymmetrical compounds using the present kinetic method.

The results clearly indicate that in phenylethylmercury the C₆H₅–Hg bond cleaves in preference to the C₂H₅–Hg bond, and that the activation energy and entropy terms are similar to those found for diphenylmercury. This would seem to indicate that the cleavage of unsymmetrical mercury compounds is a good measure of the electron availability at the attacked carbon, and not of the electronegativity of the departing group, as indicated by Kharasch. The data also clearly show that there is some transmission of electrical effects through the mercury atom, since the substitution of an ethyl group for phenyl has an effect on rate.

The cleavage of the bis-*o*-phenylenedimercury, by a two-step, consecutive competitive second-order reaction shows that strain in the molecule can reduce the activation energy—results similar to the findings for the HgI₂ cleavage.[8] It is interesting to observe that the second step involves cleavage of the –Hg– bond system so as to give phenylmercuric chloride, not benzene and bis-*o*-chloromercuribenzene. The –Hg–Cl linkage is apparently slightly electron donating, a conclusion supported by the spectral evidence of Gowenlock and Trotman,[14] in conjunction with the concepts of Doub and Vandenbelt[15] concerning displacements of the E band in *p*-disubstituted benzene compounds. These

(13) M. S. Kharasch and A. L. Flenner, *J. Am. Chem. Soc.*, **54**, 675 (1932).

(14) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1455 (1955).

(15) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

TABLE VI

$$\text{R}_2\text{M} + \text{HX} \xrightarrow[40°]{\text{Solvent}} \text{RMX} + \text{RH}$$
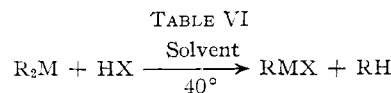
R₂M	HX	Solvent (1:10)	$k_2{}^{40}$
(C₆H₅)₂Hg	HCl	Dioxane–DMSO	0.025
(C₆H₅)₂Hg	HCl	Dioxane–DMF	.028
(C₆H₅)₂Hg	Acetic acid	Dioxane–DMF	.0047
(C₂H₅)₂Hg	HCl	Dioxane–DMSO	.00038
(C₂H₅)₂Hg	HCl	Dioxane–DMF	.0019
(C₂H₅)₂Cd	Acetic acid	Dioxane–DMF	.025

workers conclude that the –HgCl substituent is a weak *ortho–para* director.

Variation in M.—Although Gilman has reviewed the area of stability of C–M bonds by means of relative rates of addition across multiple bond linkages, no quantitative data are available concerning the rates of cleavage reactions. Table V shows the kinetic and thermodynamic data for compounds of Sn, Pb and Hg.

Taking into account the statistical factor one finds for reactivity ratios of Hg, Pb and Sn bonds the values 300:60:1. It is apparent that the decrease in reactivity is due to the increase in activation energy—this decrease in reactivity being offset to some extent by the increasing entropy term. A rough evaluation of the stability of Cd–C bonds toward cleavage may be arrived at from the data in Table VI. The approximate reactivity ratios would appear to be 50,000:300:60:1.

The data therefore reveal that it should be possible to separate Sn and Hg carbon linkages and Hg and Pb carbon linkages by selective acid cleavage. Further work in the area of carbon–metal bond stability is being conducted.

Effect of Solvent and Acid.—One of the difficulties encountered in comparing the various investigations made in the field of cleavage of organomercury compounds is the comparison of rates made in different solvent systems. In order to better understand and correlate the work in the literature an investigation of the reaction of diphenyl- and diethylmercury with hydrogen chloride

TABLE VII

Solvent

R$_2$Hg + HX $\longrightarrow$ RX + RHgX

R$_2$Hg	HX	Solvent^c	Dielectric^a constant	19	25	32	40	50
(C$_6$H$_5$)$_2$Hg	HCl	DMSO–dioxane, 10:1	26	..	0.0093	0.016	0.025	..
	HCl	DMSO–DMS–dioxane, 10:2.5:1		..	.023	.037	.071	..
	HBr	DMSO–dioxane, 10:1	26	..	.012	.021	.048	..
	HCl	DMF–dioxane, 10:1	33	..	.0066	.014	.027	..
	HCl	Dioxane	2	0.41	.58	.91	...	..
	HClO$_4$	Dioxane–H$_2$O, 35:1^b	4	..	..	..	...	0.039
	HCl	Bz–MeOH, 4:1	28	0.22	.35	.55	...	..
	HCl	Ethanol	25	..	..	.15	0.22	.44
	HClO$_4$	95% ethanol^b	25	..	..	..	.0045	.015
	HBr	Ethanol	25	..	..	.21	.32	.52
	TsOH	Ethanol	25	..	..	.055	.091	.19
	CCl$_3$COOH	95% ethanol	25	..	..	.0010	.0022	.0050
	HCl	95% ethanol	25	..	..	.0036	.0098	.030
(C$_2$H$_5$)$_2$Hg	HCl	DMSO–dioxane, 10:1	26	..	..	..	.00038	.00082
	HCl	DMF–dioxane, 10:1	33	..	..	..	.00019	.0064

Column header note: k_2, l./mole-sec., t, °C.

^{a} Sargent model V oscillometer. ^{b} T. Kaufman and A. H. Corwin, J. Am. Chem. Soc., **77**, 6281 (1955). ^{c} All solvent ratios are by volume.

and other acids in several solvent systems was made. The results are shown in Table VII, along with available data. *Where possible solvent systems were chosen to give dielectric constant values near 30.*

The results clearly indicate that there is no good correlation between the dielectric constant of the solvent and the reaction rate. It also indicates that reaction rate is not always a reliable criterion for a study of effect of solvent on rate, since in the dimethyl sulfoxide–dimethylformamide (DMF) correlation a small change in rate is observed but in actuality large changes in $E^{\neq}$ and $\Delta S^{\neq}$ are noted. A trend is noted when comparisons are made with the data of other workers—increases in energy of activation are accompanied by increases in entropy of activation. Surprisingly enough there is a linear free-energy relationship between $E^{\neq}$ and $\Delta S^{\neq}$ for the various acid systems investigated to date (Fig. 3). Such a relationship could only be valid if the solvents employed perform closely similar roles in the reactions studied. It is also necessary that the different proton donors serve a similar function in the formation of the transition state.

It is further obvious that the anion plays some important role in the rate-determining step, as the HBr, HCl–DMSO systems testify—where large changes in $E^{\neq}$ and $\Delta S^{\neq}$ result from a change from HCl to HBr.

It has been shown previously that sulfuric acid does not react with diphenylmercury in DMSO–dioxane at a rate fast enough to be measured at 0.1 M concentrations,[2c] and it is known that there is no deuterium isotope effect (DCl vs. HCl) in the same system.[2c] The latter indicates that either molecular attack of HX on diphenylmercury with little bonding of H to C in the transition state (slight bond making) is involved, or that ion pair or solvent-separated ion pair attack is involved.

The linear relationship ($E^{\neq}$ vs. $\Delta S^{\neq}$), showing as it does the dependency of the energy terms upon the solvent and anion of the attacking acid with a consideration of the above data, argues for attack by solvent-separated ion pairs. Such a suggestion

is supported by the data of Kaufman on the cleavage of diphenylmercury by HCl and HClO$_4$ in dioxane–water (7:3 by volume). The cleavage by HCl ($k_2^{50°} = 8.75 \cdot 10^{-3}$ l./mole-sec.) is almost twice as fast as that by HClO$_4$ ($k_2^{50°} = 4.84 \cdot 10^{-3}$ l./mole-sec.). The addition of KClO$_4$ in stoichiometric quantities does not affect the rate of cleavage by HClO$_4$, but the addition of stoichiometric quantities of KCl increases k_2^{obs} to the value measured for HCl, clearly a case of equilibrium between KCl and HCl.[16] Further support is derived from data indicating that the addition of chloride ion increases the rate or cleavage of diphenylmercury by HCl in DMSO, dioxane, but sulfate ion does not.[2c]

Acidity Functions.—Since these reactions involve an attack by protonic acids in non-aqueous solvents it seemed advisable to investigate the acidity functions[17] for the various systems studied. Using p-nitroaniline as an indicator, the H-values for the systems listed in Table VII were measured using the technique described by Braude.[18] The results are shown in Fig. 4. Using the concepts of Braude,[18] if the ionization constant of the acid in the solvent under consideration is large, then a plot of H versus log (HX) will be linear with unit slope. Such a relationship seems to fit the systems HCl–8 BZ–2 MeOH, HCl–EtOH, HClO$_4$–95 EtOH–5H$_2$O, HBr–EtOH, TsOH–EtOH, CCl$_3$COOH–95 EtOH–5H$_2$O, HCl–95 EtOH–5H$_2$O, and HCl–10 DMSO–2.5 DMS–1 dioxane. The sequence of limiting values of H seems reasonable, taking into account the dielectric constants, basicities and solvating abilities of the solvent systems.[18,19]

If, on the other hand, the ionization constant of the acid in the solvent under consideration is small, then a plot of H versus log (HX) will be linear with

(16) F. Kaufman, Ph.D. Dissertation, John Hopkins Univ., 1948.

(17) H, the acidity function is defined as log $((a_H{}^+f_B)/f_{BH}{}^+)$, and is the negative of H_0, the acidity function defined by Hammett.

(18) E. A. Braude, J. Chem. Soc., 1971 (1948).

(19) (a) Cf. I. M. Kolthoff and S. Bruckenstein, J. Am. Chem. Soc., **78**, 1 (1956); (b) C. A. Bunton, J. B. Ley, J. Rhind-Tutt and C. A. Veinon, J. Chem. Soc. (to be published), indicate that below 0.1 M the acidity functions of HClO$_4$ and HCl are equal in ethanol–water and dioxane–water solutions.
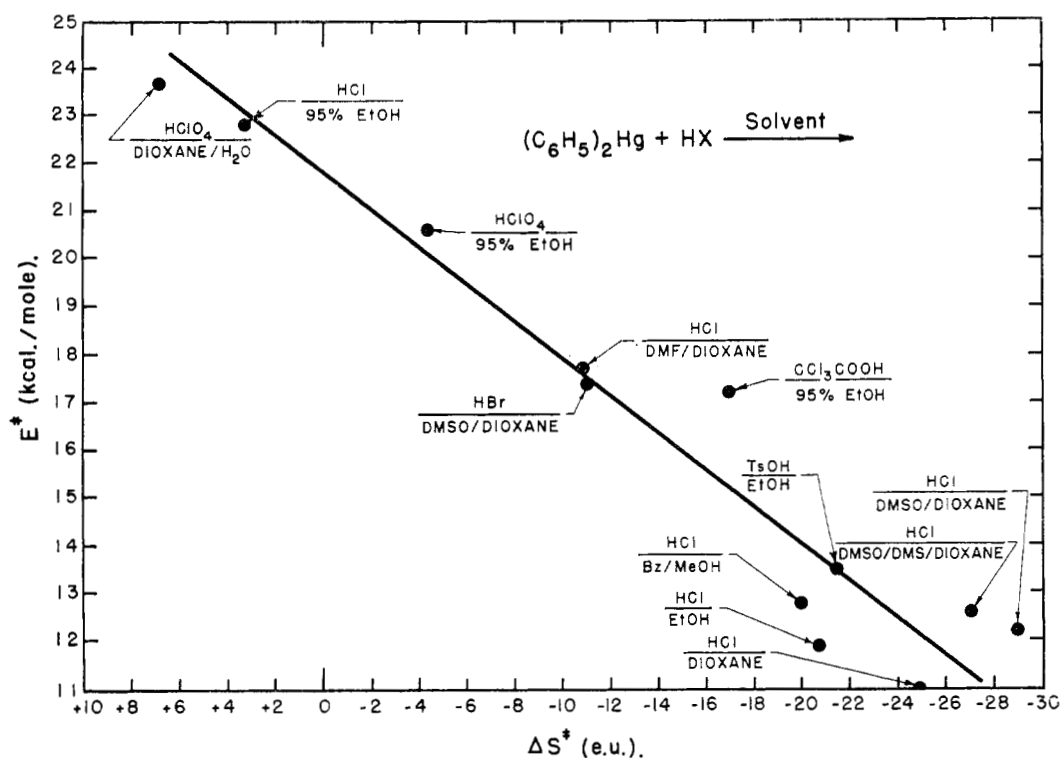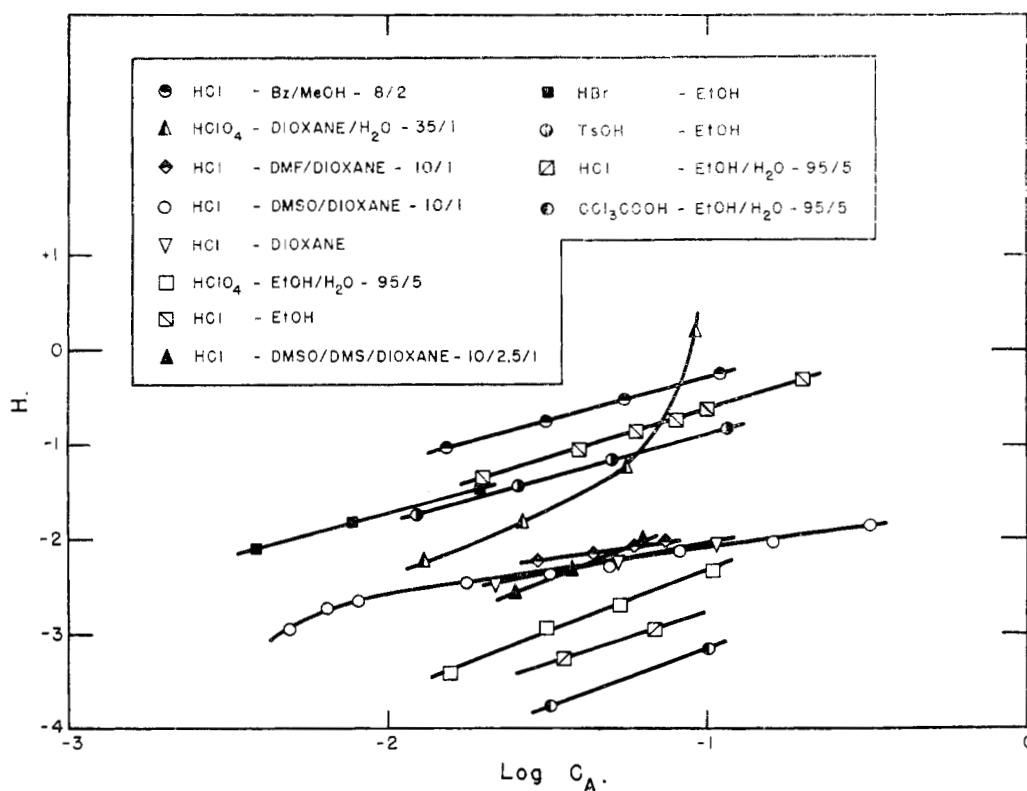
Fig. 3.

Fig. 4.

half-unit slope. Such a relationship fits the systems HCl–10 DMSO–1 Dioxane, HCl–10 DMF–1 dioxane, and HCl–dioxane; all of the systems falling approximately on the same curve.

The system HClO₄–35 dioxane–1 H₂O is anomalous, with a slope of 1.6 and this resembles HCl in nitromethane.[20]

(20) L. C. Smith and L. P. Hammett, *J. Am. Chem. Soc.*, **67**, 23 (1945).

Figure 5 shows a plot of log $k_2^{32°}$ vs. $H_{init.}$, the experimental acidity function at the initial acid concentrations, for the reaction in the various systems studied. It will be noted that except for HCl–dioxane the plot is linear with unit slope.

$$(C_6H_5)_2Hg + HX \xrightarrow{\text{Solvent}} C_6H_5HgX + C_6H_5H$$
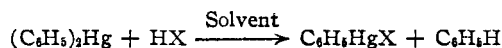
Such a relationship is to be expected for an A — S_e2 reaction,[21] and further supports the concept of attack by solvent separated ion pairs.

The log k_2 vs. H relationship can be seen as follows: Although

$$H = \log K_I^s/K_I^{H_2O} + \log \alpha (HX)_{stoich}[22]$$

thus making H dependent upon α and K_I^s, the kinetic picture, demanding ion pair acid, will also be a function of the ability of HS^+, X^- to donate a proton, a task that K_I^s measures.

The deviation shown by the HCl–dioxane system is felt to be due to actual attack by molecular HCl. The low dielectric constant of the solvent makes such species as molecular HCl extremely possible.

$E^{\ddagger}$ vs. $\Delta S^{\ddagger}$.—Returning to the free energy plots shown in Figs. 1 and 3, it is easy to see that all of the investigations to date on the reaction where Z is a substituent, R is a connecting group (either —C≡C— or direct bonding), HX is an acid and

$$\left(Z \underset{}{\overset{}{\bigcirc}} -R- \right)_2 Hg \xrightarrow[\text{HX}]{\text{solvent}} \qquad (6)$$
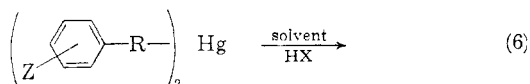
the solvents are those previously discussed, indicate that $E^{\ddagger}$ is a linear function of $\Delta S^{\ddagger}$, within a given system—*i.e.*, constant solvent, constant connector, constant substrate mercury. The dotted line in Fig. 1 is the plot from Fig. 3—representing the relationship between different solvents and acids. For *all* of the systems indicated—a total of some 30 representing the complete gamut of change of

(21) The reaction is not truly acid catalyzed of course, since acid is consumed in the reaction, but the nomenclature of acid catalysis has its usual significance otherwise. It should be noted also that H does not change markedly during the first 50% of the reaction where kinetics were measured.

(22) K_I^X represents the equilibrium constant for the exchange $XH^{\oplus} + I \rightleftharpoons IH^{\oplus} + X$.
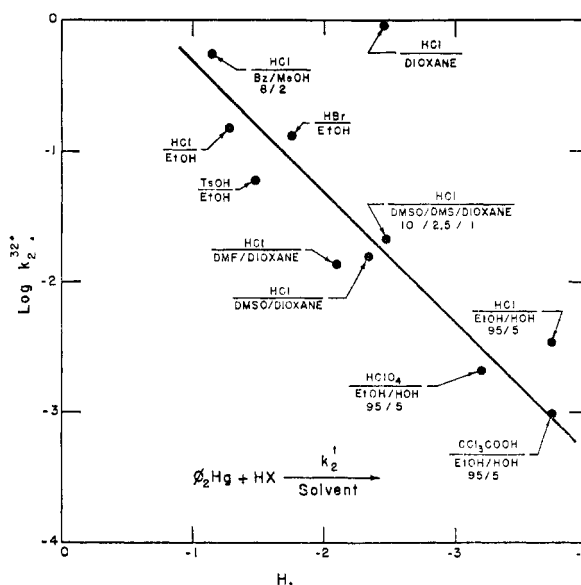

Fig. 5.

variables—a linear relationship is detected, where $E^{\ddagger} \cong 0.4\Delta S^{\ddagger} +24$. If $\Delta S^{\ddagger}$ and $E^{\ddagger}$ did not compensate for each other the reaction rates would change by a factor of 10^{15} from one extreme to another. In the present case the variation is about $10.^5$

Such free energy relationships have been discussed by Hinshelwood[23] and Leffler.[24]

It is noteworthy that this reaction of organo-metals with various acids in various solvent systems is one of the few cases that permits a correlation of acidity functions, thermodynamic quantities and reaction rates in non-aqueous or mixed solvent systems.

(23) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937).

(24) K. Leffler, *J. Org. Chem.*, 20, 1202 (1956).