5° lower than the analytical samples and over a range of 4–5°. The infrared spectra of all compounds isolated by the procedure described were identical with those of the analytical samples.

The following acetylferrocenes which have not previously been reported were isolated and characterized.

2-Acetyl-1,1′-bis-methoxyphenylferrocene was an oil. It was purified for analysis by chromatography on alumina employing ether as eluent.

Anal. Calcd. for $C_{26}H_{24}O_3Fe$: C, 70.9; H, 5.4. Found: C, 71.2, 70.5; H, 5.6, 5.6.

Its 2,4-dinitrophenylhydrazone melted at 158–159°

Anal. Calcd. for $C_{32}H_{28}O_6N_4Fe$: C, 61.9; H, 4.5; N, 9.0. Found: C, 62.5; H, 4.5; N, 9.2.

3-Acetyl-1,1′-bis-*p*-methoxyphenylferrocene was recrystallized for analysis from cyclohexane to give red block-shaped crystals, m.p. 147–148°.

Anal. Calcd. for $C_{26}H_{24}O_3Fe$: C, 70.9; H, 5.4. Found: C, 70.8; H, 5.5.

2-Acetyl-1,1′-bis-*p*-bromophenylferrocene.—Recrystallization of this compound from Skellysolve B gave red crystals, m.p. 126.5–127.5°.

Anal. Calcd. for $C_{24}H_{18}OBr_2Fe$: C, 53.53; H, 3.35. Found: C, 53.71; H, 3.55.

3-Acetyl-1,1′-bis-*p*-bromophenylferrocene was recrystallized from Skellysolve B to give red crystals, m.p. 145–147°.

Anal. Calcd. for $C_{24}H_{18}OBr_2Fe$: C, 53.53; H, 3.35. Found: C, 53.9; H, 3.2.

1-Acetyl-1′-*p*-methoxyphenylferrocene was recrystallized for analysis from low boiling petroleum ether (38–52°) to give orange-red plates, m.p. 97–98°.

Anal. Calcd. for $C_{19}H_{18}O_2Fe$: C, 68.3; H, 5.4. Found: C, 68.7; H, 5.3.

2-Acetyl-1-*p*-methoxyphenylferrocene was recrystallized from Skellysolve B as an orange microcrystalline powder, m.p. 137–139°.

Anal. Calcd. for $C_{19}H_{18}O_2Fe$: C, 68.3; H, 5.4. Found: C, 68.7; H, 5.5.

Clemmensen Reduction of 3-Acetyl-1,1′-diphenylferrocene.—The ketone (240 mg., 0.63 mmole) was dissolved in 30 ml. of glacial acetic acid, and to this solution was added amalgamated zinc, prepared from 414 mg. of zinc dust (0.64 mmole), and 1 ml. of concentrated hydrochloric acid. The reaction mixture was stirred magnetically and heated at 100° for a period of 30 minutes, then cooled and poured into a saturated solution of sodium chloride containing sodium bisulfite. The aqueous acid solution was extracted several times with ether until these extracts were colorless. The extracts were combined, washed twice with saturated sodium chloride solution, then once with sodium carbonate solution to a *p*H of 8, and finally with saturated sodium chloride to neutrality. The ether solution was dried over magnesium sulfate, drying reagent was filtered off, and the organic solution was concentrated to a volume of about 5 ml. Chromatographic purification of this material on 30 g. of alumina employing ether as eluent afforded 100 mg. of unreacted ketone and 100 mg. of 3-ethyl-1,1′-diphenylferrocene (XIII). An analytical sample, m.p. 88–90°, was prepared by rechromatographing the above material twice on short alumina columns employing petroleum ether (b.p. 20–40°) as eluent.

Anal. Calcd. for $C_{24}H_{22}Fe$: C, 78.7; H, 6.0. Found: C, 78.8; H, 5.8.

Calculations.—The quantities used in the calculations have their usual definitions[30]: $S = \int \phi_i \phi_j d\tau$, with the value of the overlap integral taken as 0.25 for adjacent 2p-orbitals $\alpha = \int \phi_i H \phi_i d\tau$; $\gamma = \int \phi_i H \phi_j d\tau$; $\beta = \gamma - S\alpha$. The overlap and resonance integrals between non-adjacent 2p-orbitals, were neglected.

The secular equation for the substituted ferrocene ring, formalized in terms of the models shown in Table V, is identical to that for fulvene. The 6 × 6 matrix, which may be factored by symmetry into one 2 × 2 and one 4 × 4 matrix, gives the molecular orbital energy levels shown in Table VI (column 1). The figures are in agreement with those calculated earlier by Pullman, Berthier and Pullman.[31]

The matrices corresponding to the secular equations for transition states, or intermediates represented by partial structures XVI and XVII are, respectively

$$\begin{matrix} A & B & 0 & 0 & 0 \\ B & A & B & 0 & 0 \\ 0 & B & A & B & 0 \\ 0 & 0 & B & A & B \\ 0 & 0 & 0 & B & A \end{matrix} \qquad \begin{matrix} A & B & 0 & 0 & 0 \\ B & A & B & 0 & B \\ 0 & B & A & B & 0 \\ 0 & 0 & B & A & 0 \\ 0 & B & 0 & 0 & A \end{matrix}$$

where: $A = \alpha - E$; $B = \beta + S\alpha - SE$.

The roots of the secular equations are given in Table VI, and these are symmetric with respect to a non-bonding molecular orbital. Localization energies were calculated in the usual fashion.[20,21]

TABLE VI

ENERGY LEVELS

Ground state	Activated complex (XVI)	Activated complex (XVII)
1.383	1.208	1.263
0.800	0.800	0.642
.535	.000	.000
− .271	− .800	− .642
−2.717	−1.208	−1.263
−3.479		

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(30) G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941).

(31) A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950).

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The Formation of Carbon–Metal Bonds

BY RAYMOND E. DESSY, WILLIAM L. BUDDE[1] AND CAROL WOODRUFF

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The reaction of monosubstituted acetylenes, $R'C \equiv CH$, with M_2HgX_4 and RHgX, leading to $(R'C \equiv C)_2Hg$ and $RHgC \equiv CR'$ has been investigated kinetically, and a four-center transition state postulated for all reactions involved. This confirms earlier suggestions made concerning the transition state for cleavage of R_2Hg compounds with HX, and suggests that the stereochemical consequences of SE2 reactions in organomercury systems are as yet unknown.

In a previous publication in this series[2] the mechanism of the cleavage of C–Hg bonds by acids was discussed in detail. In summary, it was concluded that in the cleavage of C–Hg bonds by halogen acids a four-center mechanism was in operation, involving simultaneous attack by electrophilic proton and nucleophilic halide ion. The mechanism of this reaction is of some importance since

$$\begin{matrix} C \cdots Hg \\ \vdots \quad \vdots \\ H \cdots X \end{matrix}$$

in recent years evidence concerning the stereochemical outcome of SE reactions has been derived from systems of the type C*–Hg– being cleaved

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[1] Diamond Alkali Co. Predoctoral Fellow.

[2] R. E. Dessy and J. Kim *J. Am. Chem. Soc.*, **83**, 1167 (1961).

by HgX_2 or HX. In particular, Jensen[3] has allowed optically active di-*sec*-butylmercury and di-4-methylcyclohexylmercury to react with DCl and found retention of configuration. No mechanistic investigation was attempted. Charman and Reutov[4] have investigated the disproportionation reaction between optically active di-*sec*-butylmercury and $HgBr_2$ and also found retention of configuration; second-order kinetics (rate = $k(R_2Hg)(HgX_2)$) were obeyed. In the former case, because of the sequence of reactivities as a function of the anion in HgX_2, Br > OAc > NO_3, the reaction was classified as SE2.[4a,5] Recent work[4c] has shown that this reaction involves a four-center transition state (SF2)[5], the stereochemical outcome of which is *a priori* retention. The sequence of reactivities as a function of the anion in –HgX has been used by Charman, Hughes and Ingold[4a] in an attempt to distinguish between SE2 and SF2 mechanisms in the "one and three alkyl" exchange reactions ($RHgX + HgX_2$; $RHgX + R_2Hg$), where retention of configuration is observed. Since this is not a completely unambiguous tool, their assignment of SE2 character to these reactions is not a rigorous one.

If the acid cleavage[2,3] is also definitely four center (SF2), as has been concluded, then *no* definite conclusions may be reached at present concerning the stereochemical outcome of SE2 reactions in organomercury systems since no simple reaction having definite SE2 character has been investigated. It is the purpose of this paper to present data establishing the SF2 character of the acid cleavage of C–Hg bonds by investigating the mechanism of formation of C–Hg bonds in the reaction of mercuric halides with terminal acetylenes (eq. 1. 2a. 2b). These processes are obviously related by the principal of microscopic reversibility as the following equation indicates

$$(RC\equiv C)_2Hg + HX \rightleftarrows RC\equiv CHgX + RC\equiv CH$$

Experimental

Reagents.—1,4-Dioxane (Matheson, Coleman and Bell, spectral grade) was used without further purification. Conductivity water (Amberlite IRA-120 and IR-409 resin) was used to dilute it. Triethylamine was purified by passage through 4A Molecular Sieve and subsequent distillation, b.p. 89°. Reagent grade pyridine was used; 2,6-lutidine was treated with potassium hydroxide pellets for one week, and fractionally distilled, b.p. 142°. Commercial triphenylphosphine was recrystallized from ethanol; m.p. 80°.

2-Methoxyethanol was dried over anhydrous magnesium sulfate and distilled; the middle cut boiling at 123° was used. Cyclohexane (Matheson, Coleman and Bell, spectral grade) was used without further purification.

Phenylacetylene and hexyne-1 (Farchan Research Laboratories) were redistilled before use, and stored in sealed ampoules in the refrigerator. Deuterophenylacetylene was prepared from sodium phenylacetylide (phenylacetylene and $NaNH_2$) by hydrolysis with D_2O. Infrared analysis indicated an isotopic purity of > 90%.

Since phenylacetylene at high concentrations has a tendency to oxidize slightly, giving products which absorb near 305 mμ, all solvents were purged with oil-pumped, pre-purified nitrogen before solutions were prepared, and all voids in storage vessels were filled with nitrogen.

The mercuric iodide used was Fisher, analytical reagent, recrystallized from methanol. The potassium iodide, sodium iodide and potassium bromide employed were Fisher, analytical reagent, used without further purification.

n-Butylmercuric chloride, phenylmercuric chloride, phenylmercuric bromide and phenylmercuric iodide were prepared by cleaving the commercially available bis-organomercury compounds with a tenfold excess of reagent grade mercuric chloride, bromide or iodide. *n*-Butylmercuric chloride, recrystallized from ethanol, m.p. 127–128°; phenylmercuric chloride, recrystallized from 2:1 dioxane-methanol, m.p. 260–261°; phenylmercuric bromide, recrystallized from 1:1 dioxane–ethanol, m.p. 276–277°, and phenylmercuric iodide, recrystallized from 1:1 dioxane–ethanol, m.p. 264–265°.

m-Nitrophenylmercuric chloride was prepared according to the method described by Klapproth and Westheimer.[6] It was recrystallized from 95% ethanol; m.p. 240–242°.

Bis-phenylethynylmercury was prepared as described by Johnson and McEwen[9]; m.p. 123.5–125°.

Phenylethynylmercuric chloride was prepared by cleaving 10 g. (0.025 mole) of bis-phenylethynylmercury with 6.8 g. (0.025 mole) of mercuric chloride in 125 ml. of tetrahydrofuran, which had been previously dried over $LiAlH_4$. After standing overnight, the THF was removed, and benzene added. The pale yellow solid resulting was filtered off, and washed with benzene. Recrystallization from 2:1 benzene–dioxane gave an off-white compound, m.p. 268–270°. The yield was 6.8 g. (40%). The material analyzed for C,H correctly, and showed an infrared absorption peak at 2200 cm.$^{-1}$. Several attempts to cleave bis-phenylethynylmercury with mercuric chloride or hydrochloric acid in dioxane-water solvents, or in dioxane, ethanol or acetone from which all residual water had not been removed resulted in the production of a white solid which decomposed above 300° and which was insoluble in all but basic solvents as pyridine and DMF. The material showed no triple bond absorption peak. It is suggested that this substance and the compound recently claimed[7] to be phenylethynylmercuric chloride, which also decomposed > 300°, are both probably some addition product of mercury and water to the triple bond.

The products of the kinetic reactions were identified by C,H analysis and infrared spectroscopy. For example, in the case of the reaction of C_6H_5HgBr and $C_6H_5C\equiv CH$—, to 250 ml. of dioxane-water was added 1.02 g. (0.01 mole) of phenylacetylene, 3.58 g. (0.01 mole) of phenylmercuric bromide and 20.2 g. (0.2 mole) of triethylamine. The solution was stirred at 50–60° for 0.5 hour, and allowed to stand overnight. The flask was then chilled and 500 ml. of ice-water added. The resulting solid was filtered off, and air-dried. The crude yield was 3.03 g. (80%). The material was recrystallized from methanol; m.p. 96–97°. Mixed melting points with diphenylmercury and bisphenylethynylmercury gave significant depressions. The infrared spectrum showed an absorption peak at 2160 cm.$^{-1}$, and the entire spectrum was quite different from that of diphenylmercury or bis-phenylethynylmercury.

Anal. Calcd. for $C_{14}H_{10}Hg$: C, 44.38; H, 2.70. Found: C, 43.51; H, 2.70.

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(3) L. H. Gale, F. R. Jensen and J. A. Landgrebe, *Chemistry & Industry*, 118 (1960).

(4) (a) H. B. Charman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2530 *et seq.* (1959); (b) *cf.* O. A. Reutov, *Rec. Chem. Progr.*, **22**, 1 (1961); (c) R. E. Dessy, Y. K. Lee and J. Kim, *J. Am. Chem. Soc.*, **83**, 1163 (1961).

(5) The conceptual pictures for the mechanistic pathways for SE reactions have been described by Charman, Hughes, and Ingold[4a] as derived from analogy with aliphatic nucleophilic substitution. Their classification of SE1 and SE2 reactions is both reasonable and logical. However, the so-called SEi classification[4a] is not. SNi reactions were originally defined as "intramolecular nucleophilic changes" (W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1267 (1937)). Other workers have broadened the scope of this concept, and more clearly delineated it (*cf.* J. Hine, "Physical Organic Chemistry," McGraw Hill; New York, 1956, pp. 114, 457), but this fundamental criterion has been retained. The extension of the concept of SNi reactions to the SE case also requires that this criterion be considered. In the case of four-center type mechanisms one is also faced with the problem that from the point of view of substrate the reaction path is simultaneously electrophilic and nucleophilic, and SE or SN classification seems inappropriate. It would seem more appropriate to describe the *substitution* reactions which proceed by a *four*-center *bimolecular* pathway as SF2 reactions.

(6) W. J. Klapproth and F. H. Westheimer, *ibid.*, **72**, 4461 (1950).

(7) I. Iwai and Y. Yura, *C. A.*, **55**, 4400^{d} (1961); *Takamine Kenkyusho Nempo*, **10**, 30 (1958).

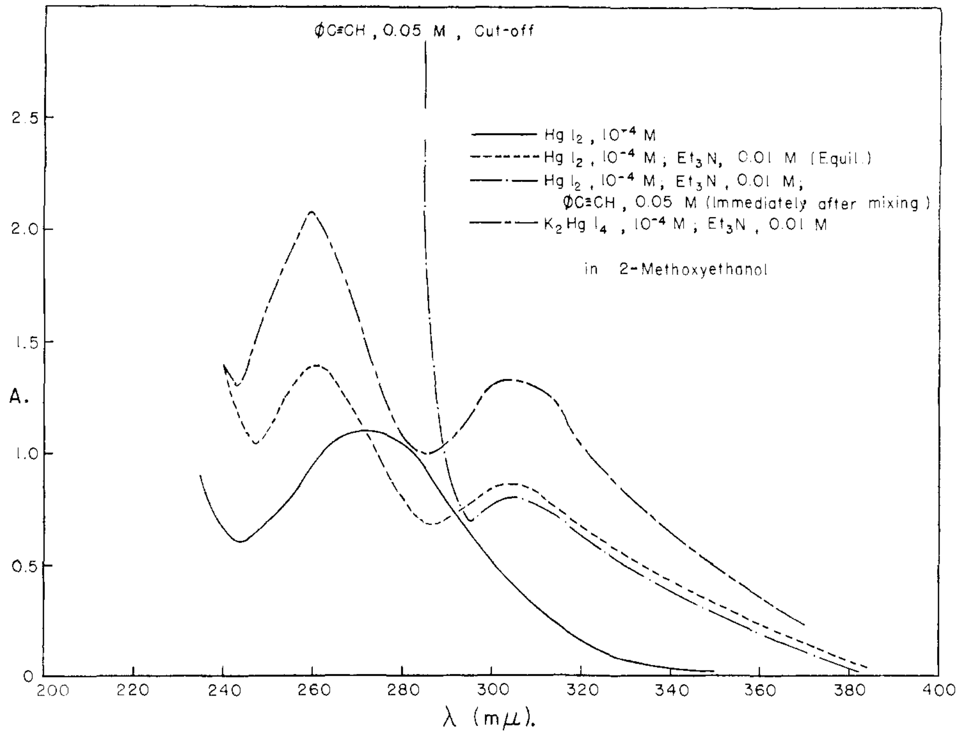

Fig. 1.

RHgX + R'C≡CH: Kinetic Method.—The most convenient method for following reactions of this type is a conductometric one. The factors RHgX and R'C≡CH and one of the products, R'C≡CHgR, show little conductance, while the $R_3NH^{\oplus}$, $X^{\ominus}$ is an excellent conductor.

A Wheatstone bridge, operating at 1000 c.p.s., and utilizing an oscilloscope as a detector was used.[2]

For a typical kinetic run, samples of the terminal acetylene, organomercuric halide and base were dissolved in 20% deionized water–80% dioxane. Prior to each rate determination the stock solutions were brought to constant temperature at 32°. Aliquots were pipetted directly into the conductivity cell, and readings of the conductivity of the thermostated solution taken as a function of time. The data were treated in the manner described below.

Calculation of Rate Constants.—The reactions were run under pseudo-second-order conditions involving large excesses of amine and equivalent concentrations of acetylene and mercuric compound. The raw data were treated according to the following integrated second-order rate equation written in terms of the resistance of the solution.

$$R_t/R_t - R_\infty = (R_0akt/R_0 - R_\infty) - (R_0/R_0 - R_\infty)$$

A plot of the left-hand side *vs.* time was made. The specific pseudo-second-order rate constant (k_2) was obtained by dividing the slope by the initial concentration and the intercept which was taken directly from the plot. Third-order rate constants were calculated from the measured pseudo-second-order constants. Good kinetic fits were obtained to 85% of completion. Most runs were made at least in duplicate.

A modified equation was utilized in those cases in which non-equivalent concentrations of acetylene and mercuric compound were studied.

M_2HgX_4 + R'C≡CH: Kinetic Method.—The most convenient method for following reactions of this type is a spectrophotometric one. At a wave length of 305 mμ, M_2HgX_4 and HgI_2 (or HgI_2, Et_3N complex) absorb (Fig. 1), while phenylacetylene, hexyne-1, triethylamine and the products bis-phenylethylnylmercury and dihexynylmercury do not. It was found that M_2HgX_4, HgI_2 and the HgI_2, Et_3N complexes obey the Lambert–Beer law in all solvents employed.

A Beckman model DU or Cary model 11 spectrophotometer equipped with thermospacers, a refrigeration unit and a photomultiplier unit was used. The entire sample area, and storage area was kept at 28°.

For a typical kinetic run, all solutions were brought to thermal equilibrium, and solvent and the solutions of alkyne, triethylamine and mercury compound were pipetted into a 10-ml. flask. The mercury compound was the last component added. The contents of the flask were used to fill the 1-cm. quartz cuvettes. Absorbancy readings were taken as a function of time, and the data treated in the manner described below.

Calculation of Rate Constants.—The reactions were run under pseudo-first-order conditions, involving large excesses of triethylamine and acetylene. Third-order rate constants were calculated from the measured pseudo-first-order constant, and the other reagent concentrations.

For those reactions involving M_2HgX_4, the rate constant can be evaluated from plots of ln *A* (absorbance) *vs.* *t*, since the only absorbing species is M_2HgX_4 (step 2 of the series pseudo-first-order reaction is rapid compared to step 1).

For those reactions involving HgI_2, two complexes which absorb may be present in addition to the HgI_2–HgI_2,Et_3N complex and HgI_2,Et_3N acetylene complex. The two complexes have absorption peaks at 305 mμ. The rate of formation of the latter is extremely fast, while that of the former varies with the solvent used—being slow compared to the reaction measured in dioxane, and about the same order of magnitude as the reaction measured in 2-methoxyethanol. If all complexes involve one molecule of HgI_2 it is easy to show that once again the pseudo-first-order rate constants may be evaluated from ln *A* *vs.* *t* plots.

$$A_t = bc_{HgI_2}[A_{HgI_2} - a_{complex}\,K(R_3N)^x(R'C{\equiv}CH)^y]$$

where $A = a'bc$, x and y are constants indicating the number of ligands per Hg, and K is an equilibrium constant; a' may be calculated from extrapolated A_0 values. It is a little surprising that where two molecules of HgI_2 seem to be involved in the complex the simple kinetic relationship is still obeyed (*cf.* 2-methoxyethanol). In any case, the method does seem to give consistent results. Good kinetic fits to 75% of reaction were obtained. Most runs were made in duplicate.

Results and Discussions

Nieuwland[8] has reported that alkylmercuric chlorides will react with acetylenes in the presence

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[8] R. J. Spahr, R. R. Vogt and J. A. Nieuwland, *J. Am. Chem. Soc.* **55**, 3728 (1933), and preceding papers.

TABLE I

$$\mathrm{RHgX} + \mathrm{HC{\equiv}CR'} \xrightarrow[\text{4:1 dioxane–}\mathrm{H_2O}]{\mathrm{R_3N}} \mathrm{RHgC{\equiv}CR'}$$

RHgX	Concn., m./l.	R'C≡CH	Concn., m./l.	R_3N	Concn., m./l.	k_3^{32}, l.²/m.²-sec.
C_6H_5HgCl	0.02	$C_6H_5C{\equiv}CH$	0.02	Et_3N	0.20	0.035
C_6H_5HgCl	.02	$C_6H_5C{\equiv}CH$	.02	Et_3N	.32	.028
C_6H_5HgCl	.02	$C_6H_5C{\equiv}CH$	.02	Et_3N	.40	.028
C_6H_5HgCl	.02	$C_6H_5C{\equiv}CH$	.02	Et_3N	.80	.024
C_6H_5HgCl	.02	$C_6H_5C{\equiv}CH$	.01	Et_3N	.20	.031
C_6H_5HgCl	.01	$C_6H_5C{\equiv}CH$	.02	Et_3N	.20	.027
C_6H_5HgCl	.005	$C_6H_5C{\equiv}CH$	.02	Et_3N	.20	.027
C_6H_5HgCl	.02	$C_6H_5C{\equiv}CH$	.02	2,6-Lutidine	.20	~ .0003
C_6H_5HgCl	.02	$C_6H_5C{\equiv}CH$	.02	Pyridine	.20	.0029
C_6H_5HgBr	.01	$C_6H_5C{\equiv}CH$	.01	Et_3N	.10	.37
C_6H_5HgBr	.01	$C_6H_5C{\equiv}CH$	.01	Et_3N	.20	.26
C_6H_5HgI	.004	$C_6H_5C{\equiv}CH$	.004	Et_3N	.04	5.05
n-C_4H_9HgCl	.02	$C_6H_5C{\equiv}CH$	.02	Et_3N	.20	0.012
$C_6H_5C{\equiv}CHgCl$	.01	$C_6H_5C{\equiv}CH$	.01	Et_3N	.20	.36
m-$O_2NC_6H_4HgCl$	.02	$C_6H_5C{\equiv}CH$	.02	Et_3N	.20	.093
C_6H_5HgCl	.02	Hexyne-1	.02	Et_3N	.20	.023
n-C_4H_9HgCl	.02	Hexyne-1	.02	Et_3N	.20	.0016
C_6H_5HgBr	.01	$C_6H_5C{\equiv}CD$	.01	Et_3N	.20	.17

of a base according to the reaction

$$\mathrm{RHgX} + \mathrm{HC{\equiv}C{-}R'} \xrightarrow{\text{base}} \mathrm{RHgC{\equiv}CR'} \quad (1)$$

It would appear that this is the second step in the familiar reaction used to characterize monosubstituted acetylenic compounds[9]

$$2\mathrm{R'C{\equiv}CH} + \mathrm{M_2HgX_4} \xrightarrow{\text{base}} (\mathrm{R'C{\equiv}C})_2\mathrm{Hg}, \text{ or} \quad (2a)$$

$$2\mathrm{R'C{\equiv}CH} + \mathrm{HgX_2} \xrightarrow{\text{base}} (\mathrm{R'C{\equiv}C})_2\mathrm{Hg} \quad (2b)$$

Kinetic procedures for following both of these reactions have been developed. and one mechanism, covering both reactions, consistent with the experimental facts can be proposed.

R'C≡CH + RHgX → : General Description.—Table I indicates the results obtained for reaction 1 under pseudo-second-order conditions (excess amine). The reaction is (a') first order in acetylene and mercuric compound; (b') the pseudo-second-order rate constant (rate = k_2(RHgX)(R'C≡CH)) is a linear function of the amine concentration and the reaction rate constant depends upon the base strength of the amine. Plots of k_2 *vs.* (Et_3N) for the C_6H_5HgCl, $C_6H_5C{\equiv}CH$ system do not quite pass through the origin (see footnote 13 for the apparent explanation); the reaction seems therefore approximately first order in amine; (c') the reaction rate constant depends upon the acidity of the acetylene,[10] (increasing as the acidity increases), and (d') on the nature of the halogen (I > Br > Cl); and (e') there is a small isotope effect (k_H/k_D = 1.5) observed when R'C≡CH is changed to R'C≡CD. Three molecules are somehow involved prior to. or during, the rate-determining process.

2R'C≡CH + M_2HgX_4 → : General Description.—Table II indicates the results obtained for reaction 2 run under pseudo-first-order conditions (excess amine and acetylene). The reaction is (a) clearly first order in acetylene and mercuric halide (or mercuric halide complex); (b) the reaction is first order in amine and the reaction rate constant depends upon the base strength of the amine; (c) the reaction rate constant depends upon the acidity of the acetylene[10] (increasing as the acidity increases), but (d) is relatively independent of the alkali metal in M_2HgX_4 (Na *vs.* K) and of the 3rd and 4th complexed halogen as a comparison of HgI_2, K_2HgI_4 and $K_2HgI_2Br_2$ indicates; there is (e) a deuterium isotope effect (k_H/k_D = 2.5) observed when R'C≡CH is changed to R'C≡CD; finally the reaction rate is remarkably independent of the solvent, as the changes from 2-methoxyethanol to dioxane–water or dioxane indicates.

Three molecules are somehow involved prior to, or during, the rate-determining process.

The similarity of points a-e in both reaction sequences suggests that the same fundamental mechanism is involved in each case.

Several miscellaneous pieces of information need to be noted before any general conclusions concerning this mechanism can be reached, however.

R'C≡CH + RHgX → : Specific Details.—(1') The rate of exchange of phenylacetylene with D_2O in dioxane, D_2O, Et_3N solvent has been measured by a simple spectroscopic method,[10] and compared with the rate of reaction of phenylacetylene with phenylmercuric chloride under similar conditions (0.2 *M* Et_3N, 80% dioxane, 20% D_2O, 32°). The exchange reaction is one-fourth the rate of reaction of phenylacetylene with phenylmercuric chloride ($k_1^{D_2O}$ = $3.6 \cdot 10^{-5}$ sec.$^{-1}$/$k_1^{C_6H_5HgCl}$ = 14×10^{-5} sec.$^{-1}$), and indicates that it is not acetylide ion that is involved in the transition state, but molecular or ion pair acetylene.

(2') The second order kinetic plots are "good" to at least 85% completion suggesting that pre-rate-determining ionization of the organomercuric halide is not involved, an equilibrium which would be subject to mass-action effects by the halide ion

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[9] J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

[10] R. E. Dessy and Y. Okuzumi, unpublished observations, cf. *Chemical and Engineering News*, Sept. 19, 1960, p. 53.

TABLE II

$$R'C{\equiv}CH + M_2HgX_4 \xrightarrow[\text{solvent}]{Et_3N} (R'C{\equiv}C)_2Hg$$

M_2HgX_4	Concn., m./l. × 10^4	$R'C{\equiv}CH$	Concn., m./l.	Et_3N concn., m./l.	Solvent[b]	k_2^{28}, $l^2./m^2.$-sec.
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	0.05	0.01	A	0.56
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	.15	.01	A	.51
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	.25	.01	A	.52
K_2HgI_4	1	$C_4H_9C{\equiv}CH$	.50	.01	A	.11
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	.25	.01	A	.52
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	.25	.0075	A	.51
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	.05	.02	A	.48
K_2HgI_4[a]	1	$C_6H_5C{\equiv}CH$	.25	.006	A	.21
Na_2HgI_4	1	$C_6H_5C{\equiv}CH$	.25	.01	A	.44
$K_2HgI_2Br_2$	1	$C_6H_5C{\equiv}CH$	.25	.01	A	.96
K_2HgI_4	1	$C_6H_5C{\equiv}CH$	.05	.01	B	.93
HgI_2	1	$C_6H_5C{\equiv}CH$	.05	.01	A	.81
HgI_2	1	$C_6H_5C{\equiv}CH$	.10	.01	A	.94
HgI_2	1	$C_6H_5C{\equiv}CH$	.15	.01	A	.92
HgI_2	1	$C_6H_5C{\equiv}CH$	.05	.01	A	.81
HgI_2	1	$C_6H_5C{\equiv}CH$	.05	.02	A	.84
HgI_2	1	$C_6H_5C{\equiv}CH$	.05	.03	A	.90
HgI_2 (Prior equil.)	1	$C_6H_5C{\equiv}CH$	.15	.01	A	.35
HgI_2	1	$C_6H_5C{\equiv}CH$	.05	.01	B	1.58
HgI_2 (Prior equil.)	1	$C_6H_5C{\equiv}CH$	.05	.01	B	1.51
HgI_2	1	$C_6H_5C{\equiv}CH$	.15	.01	C	0.44
HgI_2	1	$C_6H_5C{\equiv}CH$	.20	.01	C	.44
HgI_2	1	$C_6H_5C{\equiv}CH$	.25	.01	C	.39
HgI_2	1	$C_6H_5C{\equiv}CH$	.30	.01	C	.38
HgI_2 (Prior equil.)	1	$C_6H_5C{\equiv}CH$	.10	.01	C	.19
HgI_2	1	$C_6H_5C{\equiv}CH$	.10	0.01 Pyridine	C	[c]
HgI_2	1	$C_6H_5C{\equiv}CD$	.10	0.01	C	0.35

[a] Plus 0.002 *M* KI. [b] A = 2-Methoxyethanol, B = 80% dioxane–20% water, C = dioxane. [c] Too slow to measure.

produced by the reaction. Apparently molecular, or ion pair mercuric halide is involved.

(3′) Table I shows that in the reaction of RHgCl with $C_6H_5C{\equiv}CH$, as the hybridization of the C attached to Hg changes from sp^3 to sp^2 to sp, the reaction rate increases (by a factor of 35) and that *m*-nitrophenylmercuric chloride reacts more rapidly than phenylmercuric chloride (by a factor of 2.5). Electron withdrawal by substituents apparently aids reaction.

(4′) The reaction rate is a function of the concentration of added triphenylphosphine. The rate constant reaches a plateau at a 1:1 molar ratio (Table III). Complexes of mercuric halides with phosphines have been noted before,[11] but few studies have been made on alkyl or aryl mercuric halides, although Gowenlock has some unpublished data on this subject.[12]

TABLE III

$$\underset{0.02\ M}{C_6H_5HgCl} + \underset{0.02\ M}{C_6H_5C{\equiv}CH} \xrightarrow[\text{dioxane–water}]{R_3N,\ (C_6H_5)_3P} C_6H_5HgC{\equiv}CC_6H_5$$

$(C_6H_5)_3P$ concn., m./l.	R_3N	R_3N concn.	k_2^{32}, $l.^2/m.^2$-sec.
0.10	Et_3N	0.10	0.310
.04	Et_3N	.16	.35
.02	Et_3N	.16	.36
.02	2,6-Lutidine	.20	.015
.02	Pyridine	.20	.13

The present results indicate the formation of a stable 1:1 C_6H_5HgCl, $(C_6H_5)_3P$ complex in solution. Attempts to isolate this compound by removal of the solvent failed, yielding only C_6H_5HgCl, and *no* symmetrized product-$(C_6H_5)_2Hg$. It should be noted that the reaction rate is still a function of the base strength.

One may conclude then that ligands to mercury which cause the metal to become more electrophilic aid the reaction. Presumably the triphenylphosphine can accomplish this by strong dπ-back bonding from mercury.[13] Although conductivity data indicate that a phenylmercuric chloride solution in dioxane–water becomes more conducting in the presence of triphenylphosphine, suggesting that the latter aids in ionization of the phenylmercuric chloride, once again the fact that the second-order kinetic plots are good to at least 85%

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(11) (a) R. S. Evans, F. G. Mann, H. S. Pieser and D. Purdue, *J. Chem. Soc.*, 1209 (1940).

(12) Prof. Brian Gowenlock, private communication.

(13) The gradual decrease observed in k_2 for the C_6H_5HgCl, $C_6H_5C{\equiv}CH$, Et_3N system as the concentration of Et_3N is increased is entirely consistent with these proposals. The amine, whose primary energetic function is associated with the acetylene (specific point 1), undoubtedly complexes with the mercuric halide to a certain extent. Attempts to investigate quantitatively this complexing in the RHgX, R_3N system in our laboratory and by Gowenlock using ultraviolet spectroscopy as a tool have failed. Gowenlock[12] has found that when ammonia is passed through a benzene solution of alkylmercuric halides a white precipitate forms. Isolation yields a material that rapidly loses ammonia, evidence for a rather easily disturbed equilibrium similar to the findings for triphenylphosphine. Since nitrogen can only donate electrons, and is incapable of being involved in dπ-back bonding, the result of increased complexing will be a decrease in the electrophilic nature of the mercury, and a decreased k_2. This type of argument is completely consistent with the slightly lower rates observed for preformed HgI_2, Et_3N complexes and $HgI_4^{=}$ as compared with HgI_2 (specific points 1 and 2).

completion suggest that these ionic species are not important in the rate-determining process.

(5′) Surprisingly, when one considers the following series of bases as "catalysts" for the reaction, bases arranged in decreasing order of base strength, triethylamine, 2,6-lutidine and pyridine, one finds that the rates of reaction are ordered in the series triethylamine, pyridine, 2,6-lutidine. This suggests that some source of front strain for the amine exists in the transition state.

$2R'C{\equiv}CH + M_2HgX_4 \rightarrow$: Specific Details.—(1) Since the reaction in the case of HgI_2 involves three species, mercuric compound, acetylene and amine, as does the reaction of RHgX, and since complex formation is difficult to evaluate in the latter, investigations were made of possible complexes formed between each pair of reactants for the $C_6H_5{\equiv}CH$, Et_3N, HgI_2 systems.

The work of West, Eglinton and Kreevoy[14] indicates that in the solvents studied hydrogen bonding between the $\equiv C{-}H$ unit and the Et_3N will exist, with high formation constants.

Using the method of Job,[15a] modified according to Vosberg and Cooper[15b] and taking measurements at several wave lengths, evidence for a 1:2 Et_3N:HgI_2 complex was found in 2-methoxyethanol, a 2:1 complex in dioxane and a 1:1 complex in cyclohexane (Table IV). In 2-methoxyethanol the rate of formation of this complex is only slightly faster (a factor of 3) than the rate of reaction of HgI_2 with phenylacetylene in the presence of amine, but in dioxane it is much slower (a factor of 100), despite the fact that the rate of reaction of HgI_2 with phenylacetylene is solvent independent. Table IV indicates the pertinent data. Equilibrium constant measurements suggest that in the solvents used for kinetic investigations complex equilibrium lies far to the left.

TABLE IV

AMINE–MERCURIC IODIDE COMPLEXES

HgI_2 concn., m./l. × 10^4	Et_3N concn., m./l.	Complex ratio Et_3N/HgI_2	Solvent	k_1^{28}, sec.$^{-1}$	K
1	0.01	1/2	2-Methoxyethanol	2.4×10^{-3}	0.25
1	.01	2/1	Dioxane	8.3×10^{-6}	0.25
1	.01	1/1	Cyclohexane	Too rapid to measure	∞

What is more important, the reaction rate constant for HgI_2, Et_3N in 2-methoxyethanol or dioxane with phenylacetylene is independent of the amount of time that elapses between the mixing of the HgI_2 and the Et_3N and the addition of the phenylacetylene. Whether the preformed complex is used (equilibrium), or the three reagents are mixed simultaneously, the kinetic picture is approximately (Table I) the same. This indicates that formation of the amine–mercury complex is not energetically important.

HgI_2 in 2-methoxyethanol exhibits no peak at 305 mμ (ε 4000) while the HgI_2, Et_3N complex does show an absorption peak at this wave length. Rapid mixing of $C_6H_5C{\equiv}CH$, Et_3N and HgI_2 in 2-methoxyethanol gives a solution having a peak at 305 mμ although good values for the latter are hard to obtain because of concurrent reaction (Fig. 1).

One may conclude that either $C_6H_5C{\equiv}CH$ catalyzes formation of the HgI_2:Et_3N complex, a rather unlikely phenomenon, or it itself becomes involved in a complex with HgI_2 or HgI_2, Et_3N. The presence of amine in the complex seems indicated since $C_6H_5C{\equiv}CC_6H_5$ and HgI_2 do not appear to complex as the ultraviolet spectrum of the mixture is a sum of the spectra of the components.

The spectrum of K_2HgI_4 in 2-methoxyethanol is unchanged by the addition of Et_3N, indicating no displacement of I^- by the amine.

(2) The presence of an 11-fold excess of KI in the reaction of $C_6H_5C{\equiv}CH$ with K_2HgI_4 in the presence of amine in 2-methoxyethanol does not materially affect the reaction rate, suggesting that a pre-rate-determining loss of iodide ion from $HgI_4^{=}$[16] is not energetically important.

The fact that the rates of reaction of HgI_2 and K_2HgI_4 with phenylacetylene are remarkably alike suggest this also (Table II). Incidentally, these correlations substantiate the conclusion, reached above on kinetic grounds, that formation of a mercurinium ion $Z{-}Hg^{\oplus}$, is not involved in the rate-determining process.

(3) A comparison of Cl and I as a departing group in the reaction indicates that $k_I/k_{Cl} = 153$.

$$C_6H_5HgX + HC{\equiv}CC_6H_5 \xrightarrow[\text{dioxane–water}]{Et_3N} C_6H_5HgC{\equiv}CC_6H_5 \quad (3)$$

Assuming that this ratio holds for compounds of the type $C_6H_5C{\equiv}CHgX$, a rough estimate of the reaction rate constant for reaction (4) may be

$$C_6H_5C{\equiv}CHgI + HC{\equiv}CC_6H_5 \xrightarrow[\text{dioxane–water}]{Et_3N} (C_6H_5C{\equiv}C)_2Hg \quad (4)$$

made, using the data in Table I.[17] This value, k_3 = 55 l.^{2} mole^{-2} sec.$^{-1}$ should be compared with that for reaction (5) k_3 = 1.5/l.^{2} mole^{-2} sec.$^{-1}$.

$$2C_6H_5C{\equiv}CH + HgI_2 \xrightarrow[\text{dioxane–water}]{Et_3N} (C_6H_5C{\equiv}C)_2Hg \quad (5)$$

This automatically suggests that reaction 5 (and therefore the more general reaction 2) takes place by a two-step process in which the second step is

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[14] (a) J. C. D. Brand, G. Eglinton and J. F. Mormon, *J. Chem. Soc.*, 2526 (1960); (b) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961); (c) M. M. Kreevoy, H. B. Charman and D. Vinard, *ibid.*, **83**, 1979 (1961).

[15] (a) P. Job, *Ann. chim.*, [10] **9**, 113 (1928); (b) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

[16] The actual species present in solutions of $HgX_2 + nMX$ is currently in controversy—*cf.* H. B. Charman, *et al.*, *J. Chem. Soc.*, 1142 (1961). The latter suggest that in dilute solution, where n = 2, X = Br, the most prevalent species is $HgBr_3^-$. The work of Marcus (*Chem. Scand.*, **11**, 811 (1957)) and Sillen (*ibid.*, **3**, 539 (1949)) would seem to support this concept. In any case, since iodide is a better complexing agent than bromide, the species present in the present work are certainly at least HgI_3^-, and in the presence of large excesses of iodide ion, certainly largely $HgI_4^{=}$.

[17] Attempts to prepare $C_6H_5C{\equiv}CHgI$ from $(C_6H_5C{\equiv}C)_2Hg + HgI_2$ failed. Reversion to the symmetrical products occurs when the solvent is removed. Only starting materials were obtained.

much more rapid than the first. The kinetic picture is of course consistent with this concept.[18]

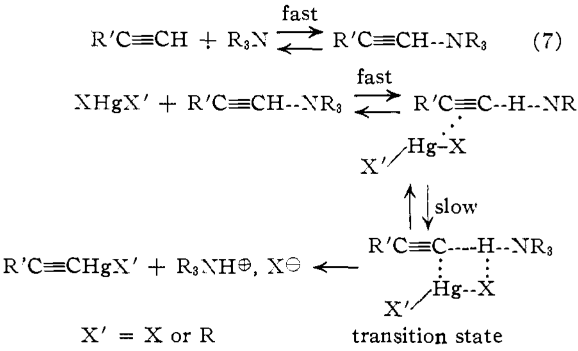
$$\begin{aligned} RC{\equiv}CH + HgX_2 &\xrightarrow{k_1} RC{\equiv}CHgX + HX \\ RC{\equiv}CHgX + RC{\equiv}CH &\xrightarrow{k_2} (RC{\equiv}C)_2Hg + HX \end{aligned} \qquad (6a)$$

This sequence is not unexpected since it is known that for the cleavage of dialkyl mercury compounds

$$\begin{aligned} R_2Hg + HX &\xrightarrow{k_1'} RHgX + RH \\ RHgX + HX &\xrightarrow{k_2'} RH + HgX_2 \end{aligned} \qquad (6b)$$

$k_1' >> k_2'$. The reaction under discussion is obviously the reverse of this sequence, and by the principle of microscopic reversibility k_2 should be larger than k_1.

Mechanism.—With these facts in mind one can postulate a mechanism for the reactions studied. The evidence surrounding reaction 2b suggests a pre-rate-determining formation of an acetylene, amine, HgX_2 complex, which in the rate-determining step "slips" from a π-"configuration"[19] to a σ- C–Hg bond and concertedly loses the elements of HX, giving $R'C{\equiv}CHgX$.



This would be compatible with general points a, b, c, e and specific points 1 and 2 listed for this reaction.

The $R'C{\equiv}CHgX'$ proceeds to react further with $R'C{\equiv}CH$ to form the observed product $(R'C{\equiv}C)_2Hg$. (This second step will be discussed below.)

Reaction 2a can be pictured in a similar manner except that pre-rate-determining loss of the 3rd (and possibly 4th) halogen occurs in a very low energy step—these halogens are known to be loosely held.[20] This would be consistent with general point d and specific point 2.

The second (fast step) of reaction 2 (reaction 1) may be pictured in a manner identical to the first step (eq. 7). This complies with general points a′–e′ and specific points 1′, 2′ and 3′ listed for this reaction. The mechanism is of course consistent with the data involving triphenylphosphine (specific point 4′) and provides a source of "front strain" for the amine in the transition state (specific point 5′). Although it is possible for a source of such front strain to be found in mercury–amine complexing, the fact that in the presence of triphenylphosphine the same base strength–rate sequence applies, makes this highly unlikely.

The reactions just considered may be termed nucleophilic displacements at a metal atom center –Hg– or as electrophilic substitution at a carbon center. They represent the reverse reaction of the system

$$R_2Hg + HX \longrightarrow RHgX + RH \qquad (8)$$

which, as mentioned earlier, seemed to involve a 4-center transition state,[2] and the reverse reaction of the system

$$RHgX + HX \longrightarrow RH + HgX_2 \qquad (9)$$

where a four-center system has been implied.[21]

In the former case[2] it has been pointed out that for a series of R_2Hg compounds, where R is varied along the series alkyl, alkenyl, aromatic and acetylenic, *i.e.*, where the attached carbon is sp^3-, sp^2- or sp-hybridized, a linear relationship between E_a and $\Delta S^{\ddagger}$ was noted—suggesting a single mechanism for the entire sequence. If a single mechanism applies to acid cleavage of C–Hg bonds, then by the principle of microscopic reversibility, a single mechanism must hold for the reverse reaction —the formation of C–Hg bonds. Although only the formation of —C≡C—Hg bonds has been studied, it is apparent that whatever mechanism is found for this system will apply to C–Hg bond formation involving sp^2- or sp^3-carbon. In the reactions of acetylenes with mercuric salts a certain amount of "π-complex" is involved where "slip" from the π- to a σ-bonded structure is postulated. However, since the effects of this complexing were not noted as a mechanistic deviation in what has been termed the forward reaction—acid cleavage of the C–Hg bond—it could represent at most a shoulder on the potential energy surface of no great significance, and hence could not affect materially the back reaction—formation of the C–Hg bond.

Therefore, this study of the back reaction confirms definitely the four-center (SF2) nature of both processes, and indicates that the C–Hg system is a poor place to search for evidence concerning the stereochemistry of the SE2 reaction. Cram's work[22] on SE1 reactions involves a very complex system, and the recent work of Brown[23] on acid cleavages in the C–B system, involves an electron-deficient metal atom where four-center attack is invited.

Obviously further work on the stereochemistry of SE reactions is needed—particularly in the C–M bond system.

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(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 165.

(19) *Cf.* the mercurinum ion proposed by Lucas] H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **77**, 939 (1955)].

(20) Data from J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1957–1958.

(21) M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 5927 (1957).

(22) D. J. Cram and P. Haberfield, *ibid.*, **83**, 2363 (1961), and preceding articles.

(23) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).