

in authentic benzalacetophenone. The mass spectrum showed 0.3% d_2 , 97.2% d_1 and 1.4% d_0 material.

cis-Benzalacetophenone was prepared by the reduction of phenylbenzoylacetylene, using Lindlar catalyst; m.p. 45.8–46.9°.

Sulfuric acid- d_2 was prepared by cautiously distilling sulfur trioxide into deuterium oxide.

Chalcone- α - d_1 in Sulfuric Acid-Dioxane Solution.—To a solution of 8 ml. of 9.0 *M* sulfuric acid in 12 ml. of dioxane was added 0.3 g. of chalcone- α - d_1 . The solution was maintained at 50° for 75 minutes, cooled to room temperature and extracted with three 30-ml. portions of ether. The ether was removed under reduced pressure, and the residue crystallized from aqueous ethanol. The product obtained weighed 0.13 g. (43%), m.p. 55.4–56.2°. The infrared spectrum (curve C) of this material showed no change from the spectrum of the original chalcone- α - d_1 , indicating no exchange of the α -deuterium during the reaction period or the isolation procedure. The mass spectrum showed 0.3% d_2 , 98.5% d_1 and 0.9% d_0 .

The Isomerization of *cis*-Chalcone in Sulfuric Acid- d_2 -Dioxane.—To a solution of 12.42 g. of 9.08 *M* sulfuric acid- d_2 (d^{22} , 1.5795) in 12 ml. of dioxane (distilled from calcium hydride) was added 0.3 g. of *cis*-chalcone. The resulting homogeneous solution was maintained at 50° for 72 minutes, cooled to room temperature and extracted

with three 30-ml. portions of ether. The combined extracts afforded an oily product after removing the solvent *in vacuo*. The crude chalcone was crystallized from aqueous ethanol; m.p. 56.6–57.3°, yield 0.129 g. (43%). The infrared spectrum of this material (curve D, Fig. 1) was completely superimposable upon the spectrum of authentic *trans*-chalcone, indicating that *no* deuterium had been introduced during the isomerization process.

Kinetic Measurements.—The rate of isomerization of *cis*-benzalacetophenone was measured as described previously,¹ by following the changes in ultraviolet absorption with a Beckman DU spectrophotometer equipped with a thermostated cell compartment. Solutions were prepared by taking sulfuric acid of the desired concentration and adding the requisite amount of a solution of *cis*-chalcone in dioxane.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We wish also to express our appreciation for the assistance of the Shell Development Co. in determining the mass spectral data reported.

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

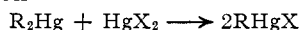
The Mechanism of the Reaction of Mercuric Iodide with Bis-organomercury Compounds

BY RAYMOND E. DESSY, Y. K. LEE¹ AND JIN-YOUNG KIM¹

RECEIVED DECEMBER 17, 1959

The rates of reaction of diphenylmercury with mercuric iodide in a variety of solvents, and a comparison of the ultraviolet spectra of the starting materials and the thermodynamics of reaction lead to some interesting conclusions concerning transition state shape. Phenylethylmercury has been found to react with $\text{Hg}^{203}\text{Cl}_2$ to yield statistical distribution of tag in the products, $\text{C}_6\text{H}_5\text{HgCl}$, EtHgCl —distribution which, it is shown, must have occurred in the transition state. By comparison with reactions of mercuracycloheptane and bis-*o*-phenylenedimercury, a transition state consistent with all of the known facts is presented.

During the past few years considerable effort has been expended^{2–5} on the elucidation of the mechanism of the electrophilic substitution that occurs in the reaction



The work of Winstein,² Jensen⁴ and Charman⁵ indicates that the substitution occurs with retention of configuration at the attacked carbon, and there seems to be little doubt that the reaction indeed involves front-side attack.³

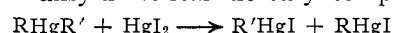
Charman⁵ has described possible mechanisms for the reaction which he terms SE1, SE2 and SEi.

Dessy and Lee⁶ suggested that the reaction involves a four-center transition state arising from molecular or ion pair attack.

In all of the investigations to date the effect of the solvent upon the shape of the reacting species has been neglected. Wright⁷ has shown by dipole moment measurements that the bis-organomercury compounds are not linear in most solvent systems,

and indeed exhibit a C–Hg–C bond angle of approximately 120°, even in non-coordinating solvents such as benzene.

In addition, a kinetic investigation of the reaction of an unsymmetrical mercury compound has



not been attempted—an investigation which should shed some light on the controversy concerning the electronegativity sequence established by Kharasch.⁸

Experimental

Kinetics.—The kinetic measurements were made as previously described.⁶

Solvents.—Spectral grade dioxane and cyclohexane, and analytical reagent ethanol and benzene were used throughout the investigation. They were purified by passage through 4X Molecular Sieve, Linde Co.

Organomercury Compounds.—Diphenylmercury: Distillation Products Industries No. 3868, recrystallized from ethanol; diethylmercury, prepared as previously described.⁹

Phenylethylmercury: Ethylmercuric chloride (26.5 g., 0.1 mole) was slowly added to 0.1 mole of phenyllithium (prepared from phenyl bromide and lithium) in 200 ml. of ether–benzene at 0°. The reaction was allowed to proceed at 0° overnight, and then hydrolyzed with water–ice. The organic layer was taken up in excess ether, dried over sodium sulfate, and filtered. Removal of solvent and distillation under reduced pressure yielded 13.0 g. (0.042 mole, 42%) of phenylethylmercury, b. p. 107–108° (5 mm.). Infrared

(8) M. S. Kharasch and A. L. Flenner, *J. Am. Chem. Soc.*, **54**, 576 (1932).

(9) R. E. Dessy and G. F. Reynolds, *ibid.*, **81**, 2683 (1959).

(1) National Science Foundation Predoctoral Research Fellows.

(2) S. Winstein, T. G. Traylor and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955).

(3) S. Winstein and T. G. Traylor, **78**, 2597 (1956).

(4) F. R. Jensen, L. H. Gaile, L. D. Whipple and D. K. Wedergaertner, Abstracts, 135th Meeting of the American Chemical Society, Boston, Mass., April 5th–10th, 1959, p. 80-O; *ibid.*, **81**, 1262 (1959); **82**, 2469 (1960).

(5) H. B. Charman and C. K. Ingold, *J. Chem. Soc.*, 2523, 2530 (1959).

(6) R. E. Dessy and Y. K. Lee, *J. Am. Chem. Soc.*, **82**, 689 (1960).

(7) H. Sawatzky and G. Wright, *Can. J. Chem.*, **36**, 1555 (1958).

TABLE I
 Solvent
 $(C_6H_5)_2Hg + HgI_2 \rightarrow 2C_6H_5HgI$

Solvent	ϵ^{20} (dielectric constant)	Base strength ^a	k_{21} , l./mole-sec.				E^\ddagger , kcal./ mole	ΔS^\ddagger , e.u.	C_6H_5Hg		HgI_2	
			15	25	35	45			λ_{max} , m μ	log ϵ	λ_{max} , m μ	log ϵ
Dioxane	2.3	↑	..	2.00	3.90	7.60	12.8	-16	225	4.42	270	3.74
Ethanol	25		32.1	62.8	113.0	..	11.7	-13	226	4.28	271	3.74
Benzene	2.3		19.0	29.2	43.0	..	7.6	-28	276	3.76
Cyclohexane	2.0		..	15.9	23.2	34.0	7.6	-31	231	4.46	276	3.67
									261	3.03		

^a E. Braude, *J. Chem. Soc.*, 1971 (1948).

spectral analysis indicated absorption typical of both diphenyl and diethylmercury in the 3-9 μ region and the following absorption peaks in the "fingerprint" region typical of the unsymmetrical compound: 950(w), 810(w), 750(s), 740(s) cm^{-1} .

Anal. Calcd. for $C_8H_{10}Hg$: C, 31.32; H, 3.29. Found: C, 32.24; H, 3.30.

Treatment with mercuric chloride yielded a white solid which when extracted with hot methanol left a solid that recrystallized from excess methanol and proved identical with phenylmercuric chloride (m.p., mixed m.p. and infrared spectra).

Dipole moment measurements, performed by Wright and Sawatzky (cf. reference 7) indicated the following values in benzene at 20°.

Compound	μ , D.
$(C_6H_5)_2Hg$	0.72
Et_2Hg	0.55
C_6H_5HgEt	1.09

The above data seem to confirm the synthesis of an unsymmetrical stable organomercury compound.

Mercuracycloheptane was prepared as previously described.⁷

Bis-*o*-phenylenedimercury, donated by the Orgmet Co., Wenham, Mass., was recrystallized from DMF.

Di-*n*-propylmercury was prepared as previously described.⁹

Exchange Reactions. (A).—Labeled $HgCl_2$ - Hg^{203} , obtained in the form of $Hg(NO_3)_2$ in HNO_3 from the Atomic Energy Commission, Oak Ridge, Tenn., was used as a tracer. It had the following specifications: specific activity, 1300 mc./g.; normality HNO_3 , 4.31 *N*; concentration, 18.6 mc./ml. The material was converted to $HgCl_2$ by the following procedure: 10 λ of the high specific activity $Hg(NO_3)_2$ solution was added to 2 ml. of 12 *N* HCl, and heated to dryness. The material was then heated to 120° at 3 mm. for 15 minutes. Ten grams of $HgCl_2$ was dissolved in 50 ml. of methanol, and added to the above residue.

(B) **Phenylethylmercury with Mercuric Chloride.**—To 2 mmoles of Hg^*Cl_2 in 3 ml. of methanol, prepared as indicated above, was added 2 mmoles of phenylethylmercury. A white solid precipitated immediately. Boiling methanol, 40 ml., was added, and the mixture refluxed for 15 minutes. The hot solution was filtered and the solid washed with two 50-ml. portions of boiling methanol. The material was then recrystallized from methanol giving a product that proved identical with phenylmercuric chloride (m.p., mixed m.p. and infrared spectra).

This separation depends upon the differential solubility of ethyl- and phenylmercuric chloride in methanol.

The phenylmercuric chloride was counted as an infinitely thin sample using a type TGC2 Geiger Tube (Tracerlab, Inc.) in conjunction with a Nuclear Chicago model 182 Scalar; Hg^{203} has a $t_{1/2}$ of 48d. and decays *via* β^- -0.208 Mev., γ -0.279 Mev.¹⁰

(C) **Phenylmercuric Chloride with Mercuric Chloride.**—Phenylmercuric chloride (0.67 mmole) was dissolved in 30 ml. of methanol and 0.67 mmole of Hg^*Cl_2 in methanol, prepared as indicated above, was added. The solvent was partially removed by boiling for 15 minutes and upon cooling phenylmercuric chloride precipitated. It was

(10) C. Friedlander and J. Kennedy, "Nuclear and Radiochemistry," J. Wiley and Sons, Inc., New York, N. Y., 1949.

recrystallized from methanol and counted as indicated above.

(D) **Phenylmercuric Chloride with Ethylmercuric Chloride.**—Phenylmercuric chloride (230 mg.), obtained from the reaction of diphenylmercury with mercuric chloride described above, was mixed with 230 mg. of unlabeled ethylmercuric chloride in 60 ml. of methanol. The phenylmercuric chloride was isolated as before, and assayed as indicated above.

Results and Discussion

Previous work on the reaction of diaryl- and dialkylmercury compounds with HgX_2 indicated an SE_2 mechanism involving a four-center transition state.^{4,6} Since the materials involved have been shown to be solvated, and the C-Hg-C bond angle is not the expected 180° angle, it was felt that an investigation of the rates of reaction of diphenylmercury with mercuric iodide in various solvents would aid in elucidating the mechanism more completely. Therefore the reaction was run in four solvents, solvents chosen for varying degrees of dielectric constant and solvating ability. The properties in question are listed in Table I. In addition the rates of reaction at several temperatures, and the calculated E^\ddagger and ΔS^\ddagger terms are also listed. It is interesting to note that the thermodynamic terms break the series into two convenient groups, one involving high E^\ddagger and ΔS^\ddagger , the other low E^\ddagger and ΔS^\ddagger , despite the fact that the apparent rates are in no particular ordered sequence because of the compensating effects of E^\ddagger and ΔS^\ddagger .

Wright has shown that the dipole moments, and presumably the C-Hg-C angle, varies for diphenylmercury as a function of the solvent and temperature. It is obvious that coordinating solvents such as dioxane and alcohol should complex more readily with the open mercury octets of both the diphenylmercury and mercuric iodide. In diphenylmercury this should result in a change in the hybridization of Hg from the expected sp toward sp^3 , thus reducing first possible resonance interaction of the rings (sp^2), and secondly reducing the resonance interaction of the Hg p-orbitals and the rings (sp).¹¹ Ultraviolet spectra indicate that in alcohol the resonance interaction of the phenyl groups is negligible as comparisons in Table I and II indicate, as fact previously pointed out by Gowenlock.¹² The similarity of the spectra of C_6H_5HgCl and C_6H_5HgBr indicate little transmission through the Hg atoms. The 260 m μ band is at-

(11) Cf. R. E. Dessy and Jin-Young Kim, *J. Am. Chem. Soc.*, **82**, 686 (1960).

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

tributable to the B band of benzene, while the 220 $m\mu$ band is apparently associated with both the ring and covalently bonded Hg, since the expected E_{1u} band of the phenyl group is also found at 209 $m\mu$ ($\log \epsilon = 4.28$), and CH_3HgCl and HgCl_2 both show absorption in the region¹² but with lower intensity. This is confirmed by the slightly lower intensity of phenylethylmercury as compared to diphenylmercury in the 220 $m\mu$ region—the ϵ -value of diphenylmercury is approximately twice that of phenylethylmercury, indicating that the absorption is additive.

TABLE II
ULTRAVIOLET ABSORPTION MAXIMA

Compound	$\lambda_{\text{max}}, m\mu$	$\log \epsilon$	Solvent
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5^a$	252	4.6	EtOH
$\text{C}_6\text{H}_5\text{CH}_3^a$	260	2.4	EtOH
$(\text{C}_6\text{H}_5)_2\text{CH}_2^a$	260	2.7	EtOH
$(\text{C}_6\text{H}_5)_2\text{Hg}^b$	209	4.28	EtOH
	226	4.38	
	261	2.90	
$(\text{C}_6\text{H}_5)_2\text{Hg}^b$	225	4.42	Dioxane
	260	2.95	
$\text{C}_6\text{H}_5\text{HgC}_2\text{H}_5^b$	220	4.11	Dioxane
	260	No definite peak	
$\text{C}_6\text{H}_5\text{HgX}^a, b$	212	4.12	EtOH
(X = Cl, Br, CN)	258	2.46	
CH_3HgCl^a	206	3.17	EtOH
HgCl_2^a	211	3.60	EtOH
HgI_2^b	215	4.36	EtOH

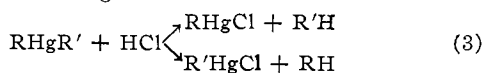
^a B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1455 (1955). ^b Present work.

In any case, it is interesting to note that non-coordinating solvents such as cyclohexane result in bathochromic shifts in the 220 $m\mu$ band which would be expected if the diphenylmercury is more planar, and is therefore capable of exhibiting more phenylmercury resonance interaction, in such solvents when compared with methanol or ethanol. The 260 $m\mu$ band is not shifted in wave length, apparently because the rings are operating independently of the mercury atom.

Such a conclusion seems to fit well with the thermodynamic data for the reactions. It would be expected that the highly polar transition state would be solvated to a similar extent in all four solvents studied, and that materials which solvated the ground states well would involve a larger ΔS^\ddagger than those in which solvation in the ground state was poor, where transfer to the transition state would involve a larger "freezing out" of solvent. On the other hand, the solvation in the ground state would tend to lower the energy of this state, leading to higher activation energies for solvated factors. Both of these conclusions are realized.

A similar explanation of course fits the other substrate, HgI_2 .

In 1932, Kharasch⁸ published the results of an intensive investigation of the reaction



which indicated that the ease of cleavage of the $-\text{C}-\text{Hg}$ bond, under these conditions, is $\text{C}_6\text{H}_5 > \text{Me} > \text{Et} > i\text{-Pr}$. It was felt that it would be of

interest therefore to examine the reaction



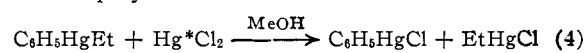
and compare it with the reactions of the related symmetrical compounds previously measured. Table III lists the kinetic data found for diphenyl-, diethyl- and phenylethylmercury, along with polarization and dipole moment data. It should be noted that all changes of reactivity are the results of changes in ΔS^\ddagger , and that in symmetrical compounds, as expected, phenyl cleaves off more rapidly than ethyl. The rate sequence also seems to follow the order of increasing polarizability.

TABLE III

Dioxane		$\text{RHgR}' + \text{HgI}_2 \longrightarrow \text{RHgI} + \text{R}'\text{HgI}$				
R	R'	$\rho\tau, \text{cc.}^a$	$\mu^{20}, \text{B}_1(\text{D})$	$1./\text{mole-sec.}^b$	$E^\ddagger, \text{kcal./mole}$	$\Delta S^\ddagger, \text{e.u.}^c$
C_2H_5-	C_2H_5-	38	0.55	0.016	12.3 ^b	-28 ^b
C_6H_5-	C_6H_5-	68	0.72	2.00	12.8 ^b	-16 ^b
C_6H_5-	C_2H_5-	73	1.09	58.0	12.5 ^c	-11 ^c

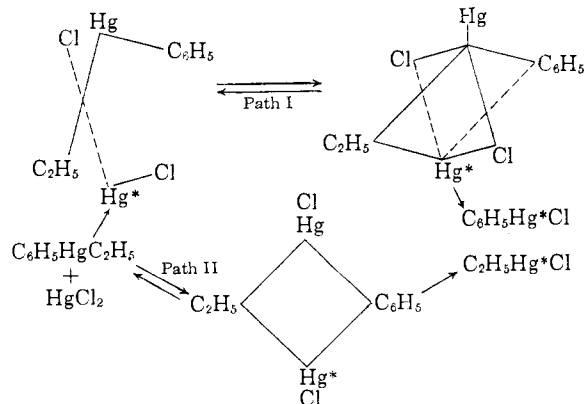
^a Courtesy of G. F. Wright. ^b See ref. 6. ^c Calculated from the data $k_2^{15} = 29.2$, $k_2^{25} = 58.0$.

It would seem logical to assume that in the reaction of phenylethylmercury it is the phenyl group which cleaves off, and to test this, radioactive Hg^{203} was employed as a tracer.



The results are described in Table IV, system 1. That the statistical exchange noted is not due to exchange after reaction between the products, or during the reaction between products and factors is shown by data from systems 2 and 3. The conclusion is therefore unavoidable. Statistical exchange occurs in the transition state, where the two mercury atoms are of necessity equivalent. Similar results have been obtained in the system *cis*-2-methoxycyclohexylneophylmercury plus Hg^*Cl_2 investigated by Winstein.¹³ No explanation was provided in these papers, and the obvious anomaly was overlooked.

It appears that only two possible simple transition states could provide for equivalency of mercury



It must be remembered that in the solvents employed the reactants are non-linear, and reaction path I is therefore reasonable. Known facts con-

(13) S. Winstein, *J. Am. Chem. Soc.*, **77**, 3747 (1955).


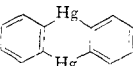
TABLE IV
CH₃OH

$$\text{C}_6\text{H}_5\text{HgEt} + \text{Hg}^*\text{Cl}_2 \longrightarrow \text{C}_6\text{H}_5\text{HgCl} + \text{EtHgCl}$$

System	Assayed material	Specific activity (c./m.-mg. Hg)		Activity ratio (average)
		Run 1	Run 2	
.....	Hg*Cl ₂	2.85	3.25	1.00
(1) C ₆ H ₅ HgEt + Hg*Cl ₂	C ₆ H ₅ HgCl	1.32	1.60	0.47
(2) C ₆ H ₅ HgCl + Hg*Cl ₂	C ₆ H ₅ HgCl	0.04	0.03	0.012
.....	C ₆ H ₅ Hg*Cl	1.32	1.60	1.00
(3) C ₆ H ₅ Hg*Cl + Et-HgCl	C ₆ H ₅ HgCl	1.31	1.59	0.99

TABLE V
Solvent

$$\text{R}_2\text{Hg} + \text{HgI}_2 \longrightarrow 2\text{RHgI}$$

R ₂ Hg	Solvent	h ₂ l./mole-sec.							E _‡	ΔS _‡
		15°	25°	35°	40°	45°	50°			
n-Pr ₂ Hg	Benzene	..	0.112	0.205	..	0.355	..	11.0	-28	
(C ₆ H ₅) ₂ Hg	Benzene	19.0	29.2	43.0	7.6	-28	
	Benzene	0.660	..	1.00	8.4	-35	
n-Pr ₂ Hg	Dioxane	..	0.019	0.035	..	0.060	..	12.2	-28	
(C ₆ H ₅) ₂ Hg	Dioxane	..	2.00	3.90	..	7.60	..	12.8	-16	
	Dioxane	k ^I	25.3	44.8	9.9	-20	
		k ^{II}	5.90	10.0	10.2	-22	

cerning the reaction—(1) second order character,⁶ (2) inhibition by I^{⊖5}, (3) lack of acceleration by H₂O⁶ and (4) NO₃ > AcO⁵ and Cl > Br > I⁶ in H_gX₂—are consistent with such a picture.

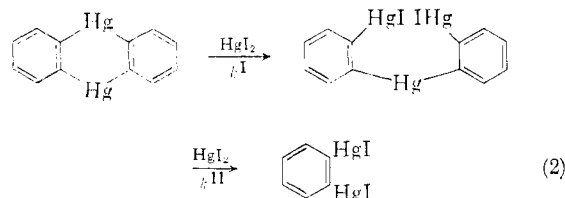
Path II involves a transition state in which transfer of a halogen to the Hg of the bis-organo-mercury and three-center bonding of the mercuries and organic radicals results in equivalent mercury atoms. It too would also be consistent with the above facts.

In order to test these possibilities two cyclic compounds containing mercury as a hetero atom have been prepared, and their rates of reaction measured.

The results are shown in Table V. Mercuracycloheptane contains mercury in an 7-membered ring. Recalling that the tetrahedral covalent radius of Hg is 1.48 Å. the hole in the hetero ring is approximately equal to that in cyclooctane. This spacing is obviously not large enough to admit a HgI₂ attacking molecule, and if path I were correct we should find a large decrease in rate when comparing the cyclic compound with a model open-chain one. Such is obviously not the case. The rates of reaction of mercuracycloheptane and di-*n*-propylmercury are almost identical. Models of mercuracycloheptane indicate that the two methylene carbon atoms which would be involved in the formation of the transition states indicated by path II are relatively exposed if one assumes a C-Hg-C bond angle of 120°. The transition state would involve little increase in strain. As one would expect, the activation energy for the cyclic compound is lower because of ring strain, while the entropy term is also lower, because of the decreased proba-

bility for proper orientation leading to the transition state. One would conclude that path II more closely approximates the route of reaction.

Similar results are found in bis-*o*-phenylenedimercury. Rate constants for both cleavage steps were obtained by the method of Frost.¹⁴



The small changes in rate, the energy and entropy relations, all favor path II.

It should be pointed out that this transition state explains the previously reported anomaly⁶ that in the reaction of a series of symmetrically substituted diphenylmercury compounds, the Hammett correlation requires only one ρ—having the form log k/k₀ = ρσ, not the form log k/k₀ = ρσ + ρ'σ', expected for four-center attack. This single low ρ-value (-5.8) is best explained by a transition state that possesses equivalent ring systems, where substituents can act equally and additively on the attacked centers.

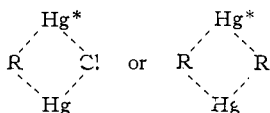
Since spectra indicate that there is little resonance interaction between groups attached to H_g, and symmetrically substituted compounds cannot by their nature yield much information concerning an inductive effect, one is faced with the question, can mercury transmit inductive effects readily? Although we are currently investigating this ability, a partial answer may be in the observed fact that phenylethylmercury reacts some 30 times more rapidly than diphenylmercury—an indication that the electrophilic cleavage is accelerated by an ethyl group and retarded by a phenyl group.

It is challenging to compare these exchange results with the data recently reported by Reutov, who has investigated the exchange between Hg²⁰³ and R₂Hg or RHgX.¹⁵ He has found under fairly mild conditions, temperatures and reaction times being some fivefold higher than the present conditions, that the mercuries do exchange, and

(14) A. A. Frost and W. Schwemer, *J. Am. Chem. Soc.*, **74**, 1268 (1952).

(15) O. A. Reutov and G. M. Ostapchuk, *J. Gen. Chem. U.S.S.R.*, **29**, 1588 (1959), English pagination.

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.

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[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 KIM¹

RECEIVED APRIL 30, 1960

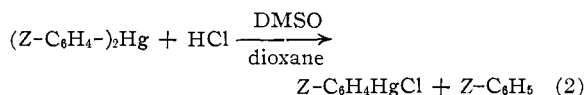
By means of an intensive investigation of the reaction $R_mMR' + HX \xrightarrow{\text{solvent}} R_mMX + R'H$ data concerning: (1) the ability of a triple bond to conduct electrical effects to a reaction site, (2) the relative stability of C-M bonds as a function of hybridization of the carbon atom, (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^\ddagger and ΔS^\ddagger , $\log k_2$ 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



has been undertaken.²

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

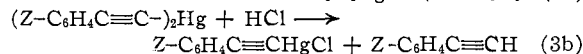


where Z is a *meta* or *para* substituent, the following facts have been observed: (a) the reaction involves electrophilic attack by molecular or ion pair HCl on the C-Hg linkage with the Hammett $\rho = -2.8$, (b) E^\ddagger is a linear function of ΔS^\ddagger .^{2a}

Considerable effort has also been expended in the past in order to determine the ability of a $-C\equiv C-$ 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 $-C\equiv C-$ 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 $(Z-C_6H_5)_2Hg + HCl \longrightarrow Z-C_6H_4HgCl + Z-C_6H_5$ (3a)



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^\ddagger and ΔS^\ddagger has been noted for the M = Hg system, spanning some 7.5 activation entropy units, and 2.5 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,⁵ 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.**

(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).

(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).