solvent. Absolute values are not known, but dipole moment measurements[10] indicate that in solvents such as dioxane, benzene or CCl_4 the angle may be of the order or 120–150°, and that it is highly dependent upon solvent and temperature.

The change in dipole moment is believed to be the result of changes in solvation around the mercury—changes which cause the normal sp-hybrid, which yields a 180° C–Hg–C bond angle, to rehybridize to something which, in a sufficiently solvating media, would approximate the tetrahedral.

Complex mercuric ions of the type $HgI_3{}^{--}$ $HgI_4{}^{--}$ are stable and the latter have been shown to be tetrahedral.[11] Mercuric iodide dissolved in dioxane also has been reported to be tetrahedral in structure. All the information seems to indicate that divalent mercury compounds have a strong tendency to accept one or two pairs of electrons, a conclusion which might be expected from the fact that Hg is one of the so-called electron-deficient elements and has 2 vacant p-orbitals.

A tetrahedral configuration would mean that mesomeric effects cannot be transmitted from one benzene ring to the other, whereas an sp- or sp^2-hybrid in a substituted diphenyl mercury would at least permit certain interaction. It has been found[12] that there is little interaction of the π-electrons of the two benzene rings of diphenylmercury in ethanol as determined by ultraviolet spectroscopy. The spectrum resembles that of $(C_6H_5)_2CH_2$, which is tetrahedral. This seems to support the solvation concept, with the hybridization of the Hg somewhere between sp^2 and sp^3.

In a polar media such as DMSO, solvation is likely to be important in determining the over-all

(10) Cf. H. Sawatzky and G. F. Wright, Can. J. Chem., 36, 1555 (1958).

(11) M. L. Delwaulle, F. Fraveois and J. Wiemann, Compt. rend., 207, 340 (1938).

(12) B. G. Gowenlock and J. Trotman, J. Chem. Soc., 1454 (1955).

entropy term. The solvation of $(Z-C_6H_4)_2Hg$ in the highly polar transition state is probably independent of the substituent, but in the ground state large differences in solvation around Hg and consequent changes in the C–Hg–C angle could be expected. The largest solvation would be expected for those molecules having electron-withdrawing groups attached–solvation in the ground and transition state would not be appreciably different, and $\Delta S^{\ddagger}$ would be fairly high: in those compounds having electron donors attached to the ring the solvation in the ground state would be low, and the amount of solvent "frozen-out" in the transition state would be large leading to a very low entropy term. Such behavior is indeed noted in the present series investigated, the highest entropy term being associated with the m-NO_2 substituent, the lowest with p-CH_3O. The effect upon the activation energy term would of course be in the opposite direction, because of the positive nature of the attacking species.

It is possible that the changing molecular geometry also affects both energy terms. One would expect the ground states of those compounds containing electron-withdrawing groups to be more "tetrahedral" around Hg than those possessing electron donors attached to the ring. The effect of changing molecular geometry on reaction rates is a subject that has not been explored to date. It seems obvious that solvation can influence hybridization., e.g., there seems to be little hesitation in thinking of R_2Mg compounds as being tetrahedral in diethyl ether. It is hoped that this suggestion will lead to further investigation in the area.
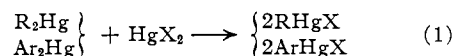
CINCINNATI, OHIO

The Mechanism of the Reaction of Mercuric Halides with Dialkyl and Diarylmercury Compounds

BY RAYMOND E. DESSY AND Y. K. LEE[1]

RECEIVED JUNE 15, 1959

The rates of reaction of a series of aliphatic and substituted aromatic organomercury compounds with mercuric halides have been measured by a convenient spectrophotometric technique in dioxane: $R_2Hg + HgX_2 \rightarrow 2RHgX$; $(Z-C_6H_4)_2Hg + HgX_2 \rightarrow 2Z-C_6H_4HgX$. In the aliphatic series (R = Me, Et, n-Pr, i-Pr) the reaction rate appears to be largely independent of R. In the aromatic series (Z = p-CH_3O, CH_3, Cl, F, C_6H_5) the Hammett equation is obeyed, $\rho = -5.87$. The addition of H_2O and $X^{\ominus}$ has little or no effect upon rate, and the observed rate sequence upon changing X is $HgCl_2 > HgBr_2 > HgI_2$. Activation energies and entropies have been measured, and in conjunction with other data indicate a four-center transition state arising from molecular or ion pair attack.

Although the reaction of a dialkyl- or diarylmercury compound with mercuric halides

$$\left.\begin{array}{c} R_2Hg \\ Ar_2Hg \end{array}\right\} + HgX_2 \longrightarrow \left\{\begin{array}{c} 2RHgX \\ 2ArHgX \end{array}\right. \qquad (1)$$

has been known and used synthetically for a

(1) National Science Foundation Research Fellow.

number of years,[2] very little is known about the mechanism of this reaction.

Winstein[3] has reported that the cleavage of cis-2-methoxycyclohexylneophylmercury by $Hg*Cl_2$ pro-

(2) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalogue Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1921.

(3) S. Winstein, T. G. Traylor and C. S. Gainer, THIS JOURNAL, 77, 3741 (1955).

ceeds with retention of configuration, and statistical distribution of the tag. Jensen[4] has shown that di-(+)-sec-butylmercury reacts stereospecifically with mercuric bromide with retention of configuration, and Charmon[5] has employed (−)-di-sec-butylmercury with similar results. He has also reported that the reaction of HgZ_2 with di-sec-butylmercury in ethanol is second order [rate = $k(HgZ_2)(R_2Hg)$] and that the rate increased as the group Z was changed in the order Br < AcO < NO₃. On the basis of these facts Charmon felt the mechanism was more appropriately written as S_E^2 rather than S_Ei. Unfortunately he did not have available the rates of reaction of the other aliphatic mercury compounds to compare with the predicted[6] sequence of t-Bu > i-Pr > Et > Me.

It is the purpose of this paper to (a) present a convenient experimental method for measuring the rate of reaction 1 in dioxane, (b) report on the rates of reaction of a series of dialkyl and diarylmercury compounds with HgI_2, (c) show the effect of changing X in HgX_2, (d) indicate the effect of changes in dielectric constant and (e) propose a mechanism for the reaction consistent with the above facts.

Experimental

Organomercury Compounds.—All of the organomercury compounds used were freshly distilled or recrystallized. The synthetic methods employed have been described previously.[7]

Dioxane.—The dioxane was purified by passing through a column of alumina, followed by distillation from sodium. In later experiments M.C.B. spectro-reagent grade was found to be satisfactory without further purification.

HgI₂.—The mercuric iodide used was recrystallized from ethanol. The other halides were reagent grade.

Preparation of Solutions.—The solid diarylmercury compounds were weighed out directly, and dissolved in dioxane. The liquid dialkylmercury compounds were weighed by the capillary tube method, and the tube then opened under the surface of the dioxane. This prevented contamination of the laboratory by poisonous dialkylmercury vapors and sample contamination.

Measurement of Rates.—The rates of reaction were followed spectrophotometrically using a Beckman DU spectrophotometer equipped with thermospacers and photomultiplier. The temperature was controlled to ±0.1°. The reaction was performed directly in the cuvette, the reactants being thermostated at the desired reaction temperature for at least 30 minutes before mixing. The initial concentration of mercuric iodide was varied from $1\cdot10^{-4}$ to $1\cdot10^{-3} M$. The concentration of bis-organomercury varied, depending upon the rate, from $1\cdot10^{-4}$ to $1\cdot10^{-2} M$.

In order to determine a suitable wave length for each individual reaction, spectra of both starting materials, and the product were taken employing a Cary model 11 spectrophotometer, wave lengths from 300–310 mμ were used.

The reactions were followed for at least 2 half-lives. Reproducibility was ±2%. All runs were made in duplicate.

Kinetics.—The mercury compounds used as reactants and those obtained as products show end-absorption spectra occurring at from 250 to 320 mμ. It proved necessary to work on the shoulders of these bands, and three cases were encountered: (I) a wave length could be found where only HgI_2 absorbed; (II), two components absorbed at the wave length chosen; and (III), reactants and products all absorbed at the wave length chosen.

(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.

(5) Reference 4. H. B. Charmon, p. 81-O.

(6) E. D. Hughes and C. K. Ingold, J. Chem. Soc., 241 (1935).

(7) R. E. Dessy and Jin-Young Kim. THIS JOURNAL, 82, 686 (1960).

Solutions of HgI_2, R_2Hg and RHgI in dioxane obey the Lambert–Beer law over the concentration range 10^{-4} to $10^{-2} M$. Because of the simple stoichiometry it was therefore an easy matter to follow the kinetics of reactions of class I and II. In the aryl series equimolar concentrations of reactants were employed. In the aliphatic series, because of the low rate constants, the concentration of organomercury was increased.

In reactions of class III, where all components absorbed at the imposed wave length, and where, because of the end absorption only one wave length was available, the following method of obtaining rate data was used.

$$A_{total} = A_{HgI_2} + A_{R_2Hg} + A_{2RHgI} \qquad (2)$$
$$= a_1bc_1^t + a_2bc_2^t + a_3bc_3^t$$

where A is the absorbance at any time, t, a_n is the molar extinction coefficient for the n_{th} component, b is the path length, and c_n^t, the concentration at time t. Since $c_1^t = c_2^t$ if $c_1^0 = c_2^0$, and $c_3^t = 2(c_1^0 - c_1^t)$, if a wave length is chosen so that $a_2 = 2a_3$ we can, after substitution, arrive at

$$A_{(HgI_2)} = a_1bc_1^t = A_{total} - 2a_3bc_1^0 \qquad (3)$$

Since a_3bc^0 is a constant we now have the concentration of HgI_2 as a function of A_{total}.

In one or two cases it proved more desirable to choose a wave length other than where $a_2 = 2a_3$. In such cases

$$c_1^t = \frac{A_{total} - 2a_3bc_1^0}{a_1b + a_2b - 2a_3b} \qquad (4)$$

In all of the cases which required the use of method III, a_1 was found or chosen to be approximately ten times as large as a_2 or a_3; thus small errors in a_2 and/or a_3 or their difference had little effect upon the measured rate.

The method used for each compound investigated is indicated in Tables I and II.

Energies of activations are good to ±0.5 kcal./mole, entropies of activation to ±2 e.u.

Since all of the absorbances at infinite time agreed within experimental error with absorbance values calculated by assuming that only the products, RHgI, were present it may be concluded that if the reaction under consideration is reversible, K is less than 10^{-2}, and k_{rev} may be ignored in this investigation. Exchange work is in progress to determine whether the reaction is reversible.

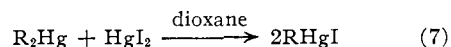**HgI₂–HgX₂ Equilibrium.**—The equilibrium constant for the reaction

$$HgI_2 + HgX_2 \underset{\longleftarrow}{\overset{K^{25°}}{\longrightarrow}} 2HgXI \qquad (5)$$
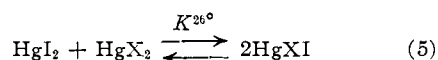
was measured by Job's method.[8] Solution of HgI_2 in dioxane and HgX_2 in dioxane were prepared, with $[HgI_2]/[HgX_2] = \rho$. Absorption measurements of mixtures of the two solutions were made at 310 mμ, where only HgI_2 and HgXI absorb. Plots of A vs. X where X is the fraction of the volume of the solution originating as HgI_2–dioxane, were made. These values of A were compared with the expected values of A predicted from the Lambert–Beer law for HgI_2, and the difference, y, between the A (calcd.) and A (exptl.) plotted against X. It can be shown[8] that at the maximum in this curve $dc_Z/dx = 0$, where c_Z is the concentration of HgXI, and that

$$K = \frac{1}{4\rho}\left[\frac{1 - X(1 + \rho)}{2X - 1}\right] \qquad (6)$$

For the present investigation a $\rho = 1/2$ was found to be convenient.

Results and Discussion

Variation in R₂Hg.—Table I lists the rates of reaction, energies of activation and entropies of activation for the reaction

$$R_2Hg + HgI_2 \xrightarrow{dioxane} 2RHgI \qquad (7)$$

where R = Me, Et, i-Pr, n-Pr, with C_6H_5 included for comparison purposes. The reactions follow second-order kinetics [rate = $k(R_2Hg)(HgI_2)$], with no indication of reversibility. It is interesting to note that within experimental error the

(8) P. Job. Ann. chim., [10] 9, 113 (1928).

TABLE I

$$R_2Hg + HgI_2 \xrightarrow{\text{dioxane}} 2RHgI$$

R₂Hg + HgX₂ Q,[a] kcal./mole		R	k_2, l./mole-sec. × 10²			$E^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.	Class[d]
HgI₂	HgCl₂		25°	35°	45°			
4.08[b]	8.47[b]	CH₃	Too slow to measure			5.95	12.3	1
6.82[c]	11.22[c]	C₂H₅	1.63	3.20	5.95	12.3	−28	I
6.62[c]	10.89[c]	n-C₃H₇	1.86	3.48	6.00	12.2	−28	I
7.93[c]	12.06[c]	i-C₃H₇	1.60	2.96	5.50	12.0	−29	III
...	...	Cyclo-C₃H₅	7.67	0.14	0.24	12.8	−22	I
...	7.71	Phenyl	197	390	760	12.8	−16	I

[a] Derived from the data of Hartley, Pritchard and Skinner[10]; the Q's represent solvated reactants and products.   [b] In ethanol.   [c] In methanol.   [d] The absorption characteristics of the reactants and products determined which kinetic method was employed.   A description of the various class methods used may be found in the Experimental section.

TABLE II

$$(Z-C_6H_4)_2Hg + HgI_2 \xrightarrow{\text{dioxane}} 2ZC_6H_4HgI$$

z	k, l./mole-sec.			$E^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.	Class[a]
	25°	35°	45°			
p-CH₃O-	71.5	......	...	..	..	II
p-CH₃-	13.1	22.7	...	10.6	−20	II
p-C₄H₅-	2.25	4.20	...	12.0	−19	III
p-H-	1.97	3.90	7.60	12.8	−16	I
p-F-	0.420	0.729	1.40	12.9	−19	III
p-Cl-	0.092	0.202	0.420	14.5	−17	III

[a] The absorption characteristics of the reactants and products determined which kinetic method was employed. A description of the various class methods used may be found in the Experimental section.

energies and entropies of activation for the sequence Et, n-Pr and i-Pr are identical. This is similar to the previous observation[9] that in the reaction

$$R_2Hg + HCl \xrightarrow{\text{DMSO-dioxane}} RH + RHgCl \quad (8)$$
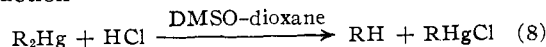
the energies and entropies of activation for the sequence Et, n-Pr and i-Pr, are almost identical.

Data on the Q's of the reactions of (C₆H₅)₂Hg, Et₂Hg and Me₂Hg with HgCl₂, HgBr₂ and HgI₂ in alcohol have been reported by Hartley, Pritchard and Skinner.[10] Although the present data do not overlap sufficiently with theirs to make quantitative comparisons, two things are evident: (a) there are significant differences in the heats of reaction of various dialkyl and diaryl-mercury compounds with mercuric halides and (b) there seems to be no consistent correlation between heat of reaction and rates. Noting that the activation energies for the groups considered are identical, and using the concepts developed by Hammond concerning the location of the transition state with respect to reactants one would conclude that the transition state, regardless of its structure, more closely resembles the reactants than the products, and that steric factors are probably not too important. It is especially interesting to observe that the entire change in the reaction rate noted when R is changed from alkyl to aryl is due to the entropy term. This is to be compared with the previously reported data in the hydrochloric acid cleavages[9] (equation 8) where the change is due to the activation energy term.

(9) Raymond E. Dessy, G. F. Reynolds and Jin-Young Kim, THIS JOURNAL, 81, 2683 (1959).

(10) K. Hartley, H. Pritchard and H. Skinner, Trans. Faraday Soc., 46, 1019 (1950); 47, 254 (1951); 48, 220 (1952).

(11) G. S. Hammond, THIS JOURNAL, 77, 334 (1955).

Variation in $(Z-C_6H_4-)_2Hg$.—Table II lists the rates of reaction and energies and entropies of activation for the reaction

$$(Z-C_6H_4)_2Hg + HgI_2 \longrightarrow 2Z-C_6H_4HgI \quad (9)$$
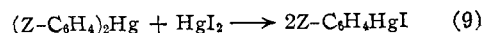
There is little doubt that the rate is enhanced by electron-donating groups, and decreased by electron-withdrawing ones, as is to be expected for an electrophilic attack. Figure 1 shows a plot of
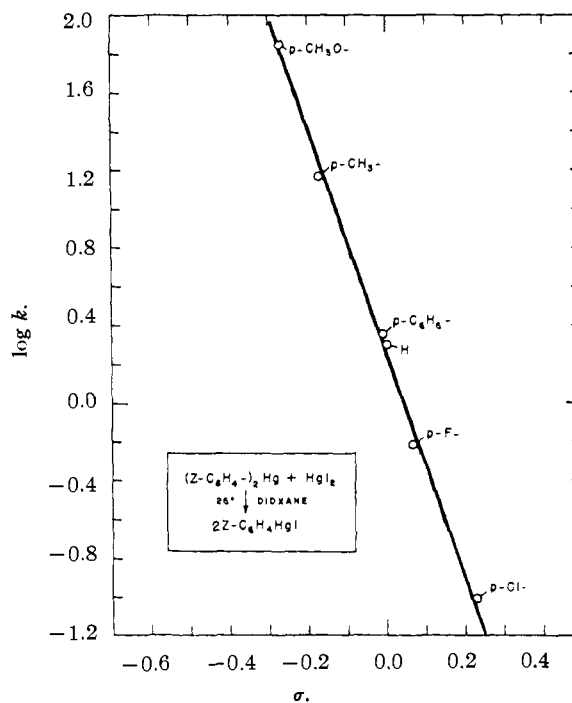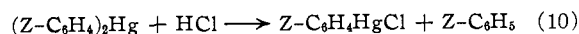

Fig. 1.—Plot of log k vs. σ for the reaction of some substituted diphenylmercury compounds with HgI₂.

log k_2[25] vs. σ, which is linear over the range studied ($\rho = -5.87$, $s = 0.16$, $r = 0.993$). This is to be compared, once again, to a similar plot[8] for the reaction

$$(Z-C_6H_4)_2Hg + HCl \longrightarrow Z-C_6H_4HgCl + Z-C_6H_5 \quad (10)$$

in which log k_2[32] vs. $(\sigma + \sigma^+)/2$ was linear ($\sigma = -2.8$).

The change in rate in the present series seems to reflect changes in energies of activation. The $\Delta\Delta S$ term is approximately 0.

Variation in Reaction Media.—Table III lists the rates of reaction for the reaction

$$(C_6H_5)_2Hg + HgI_2 \xrightarrow[H_2O]{dioxane} 2C_6H_5HgI \quad (11)$$
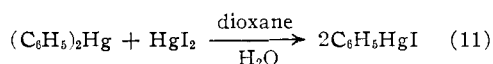
The small variations in rate seem to indicate that ionic iodide is not important in the rate-determining step. This seems to agree with the low entropy values observed for the reaction which seem indicative of a four-center reaction. Further evidence for the lack of iodide ion participation is the fact that added iodide ion (to the extent of 5 mole %), in the form of LiI, has no effect upon the rate.

TABLE III

$$(C_6H_5)_2 + HgI_2 \xrightarrow[25°]{dioxane-H_2O} 2C_6H_5HgI$$

H₂O, %	k, l./mole-sec.
0.00	1.97
0.10	2.00
1.00	2.17
5.00	3.46
10.00	6.80

Variation in HgX₂.—The rates of reaction of HgCl₂ and HgBr₂ with diphenylmercury were compared with that of HgI₂ by allowing an equal given amount of HgX₂(X = Cl, Br) and HgI₂ to compete for an insufficient amount of diphenylmercury. A plot of absorbance *versus* time for the reaction

$$(C_6H_5)_2Hg + \begin{cases} HgI_2 \\ HgX_2 \end{cases} \xrightarrow{dioxane}_{25°} \quad (12)$$
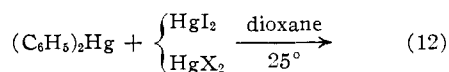
is shown in Fig. 2. The data show: 1. Mixtures of HgI₂ and HgCl₂ or HgBr₂ show lower absorbancy values than would be expected on the basis of
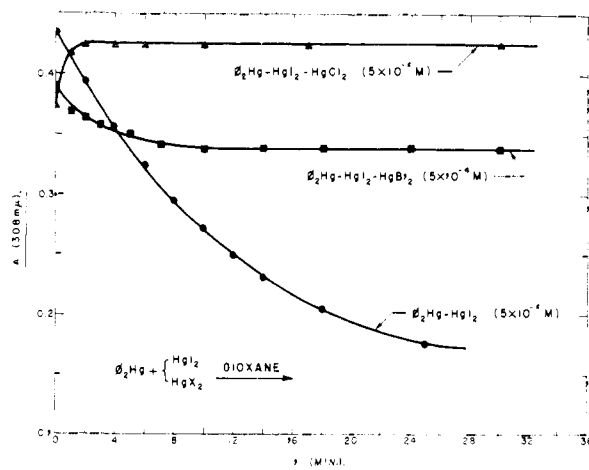

Fig. 2.—Plots of absorbance *versus* time for various diphenyl-mercury–mercury halide mixtures.

HgI₂ concentration. A mixture of HgI₂ and HgCl₂ or HgBr₂ therefore probably contains at least some of the mixed halide HgICl or HgIBr. 2. HgBr₂ reacts more rapidly with (C₆H₅)₂Hg than does HgI₂—in fact approximately 80% of the mercuric iodide remains unreacted at the end of a competitive reaction. HgCl₂ is even more reactive, leaving approximately 98% of unreacted HgI₂.

It is obvious that an equilibrium of the type

$$HgI_2 + HgX_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2HgIX \quad (13)$$
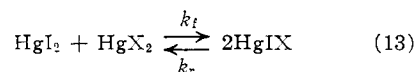
exists in the solutions examined in the competitive runs.

Examination of the equilibrium constant for this disproportionation by Job's method indicate that at 25° $K = 1$. The competitive runs indicate that k_r must be very rapid and therefore that K_f is also very rapid. This is one of the simplest disproportionation reactions studied to date, and it is interesting to observe the statistical exchange, which indicates that ΔF, ΔH and $\Delta S = 0$. In light of the differences in steric requirements and the large differences in the heats of formation of the parent HgX₂ compounds[10] this is rather surprising.

Although k_f and k_r have not been directly measured they must, of necessity, be larger than the reaction rate constant of (C₆H₅)₂Hg with HgI₂, $k_2{}^{25} = 1.97$, and in the case of HgCII faster than the reaction rate constant of (C₆H₅)₂Hg with HgCl₂, estimated to be at least 200 on the basis that only 1 to 2% of HgI₂ reacts when in competition with in equal amount of HgCl₂. Thus k_f and k_r probably have values of the order of 10³, which in dioxane is more than just surprising.
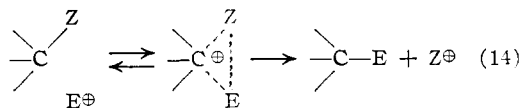
In any case the sequence of reactivities appears to be HgCl₂ >> HgBr₂ >> HgI₂. Preliminary data on other HgZ₂ compounds indicate that Hg(SCN)₂ >> HgI₂ >> Hg(CN)₂. Charmon has reported[5] that in the cleavage of di-sec-butyl-mercury the sequence is Hg(NO₃)₂ > Hg(OAc)₂ > HgBr₂.

It is interesting to note that the sequence of reactivities is approximately the same as the order of decreasing ionic character of the Hg-Z band,[12] and follows approximately the sequence of acidities of the H–Z compounds.

Mechanism.—Although, as is usually the case in mechanistic studies, it is difficult to decide on one mechanism on the basis of a particular series of experiments, regardless of how extensive this series might be, it is possible to arrive at a mechanism which is consistent with all of the above-mentioned facts.

It has been pointed out that the transition state resembles to a large extent the reactants, that in the alkyl series steric factors are not too important, and that second-order kinetics are observed in all of the cases studied.

Although the classical SN2 transition state involves backside attack of the incoming group, with the resulting inversion of the carbon center, the extension of this analogy to SE2 reactions is not obligatory. One major factor which must be considered is the fact that instead of having 5 electron pairs involved around the attacked site, as in SN2 attack, with the consequent high interaction energy, SE2 reactions involve only 4 electron pairs.[2] If one considers a front-side attack,

$$\overset{Z}{\underset{E^\oplus}{\underset{\diagup}{\overset{\diagdown}{C}}}} \rightleftharpoons \overset{Z}{\underset{E}{\underset{\diagup}{\overset{\diagdown}{C^\oplus}}}} \longrightarrow \overset{\diagdown}{\underset{\diagup}{C}} —E + Z^\oplus \quad (14)$$

(12) N. V. Sidgwick. "Chemical Elements and Their Compounds." Oxford University Press, London, 1950, p. 246.

a mode of attack which seems to be supported by the retention of configuration shown by the optically active *sec*-butylmercury compounds in their reactions with $HgBr_2$,[4,5] the above facts seem consistent. Steric factors should not, within reason, markedly affect the rate of reaction by S_E2. This has been vividly illustrated by the work of Winstein[13] on the cleavage of di-4-camphylmercury by HCl. In this case a bridge head mercurial reacts only 4 times slower than di-*n*-butylmercury.

The low entropies of activation and insensitivity to added water or iodide ion seem to support a molecular (four-center) or ion pair attack, while the large negative ρ-value for the aromatic series certainly indicates the importance of the electrophilic attack on carbon as compared to possible nucleophilic attack on mercury and points to the ready polarization of the attacking species.

The increase in rate observed in going along the sequence R, cyclopropyl, phenyl seems to be related to the entropy term. In light of the electrophilic nature of the attack this is probably related to the increased availability of electrons at the attacked position, either due to the increasing amount of delocalized π-electrons along the series or to steric factors related to hybridization of the attacked position.

It should be noted again that unlike reaction 10 which required both $\sigma + \sigma^+$ in a Hammett plot, the present reaction requires only σ. One possible explanation[14] is that the Hg atom in the attacking HgX_2 species is a very weak electrophile. It would be expected then that the rate would be quite sensitive to substituent effects, as is noted ($\rho = -5.87$); the Hg atom of the HgX_2 is appar-

(13) S. Winstein and T. G. Traylor. THIS JOURNAL. **78**. 2597 (1956).

(14) The authors wish to thank referee no. 1 for suggesting this possibility.

ently incapable of eliciting the latent electromeric properties of the substituted benzene ring (σ^+).

The linearity of the Hammett plot would seem to indicate that the effect of only one substituent is felt in the rate-determining step. If a four-center system were visualized as the activated complex

$$R-Hg-R \longrightarrow R-Hg-R \longrightarrow 2RHgX \quad (15)$$
$$X-HgX \longleftarrow X-Hg-X$$
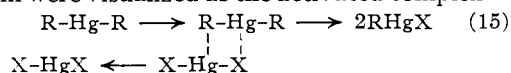
it would seem obvious that the Hammett equation relationship would be best expressed by

$$\log k/k^0 = \sigma\rho + \sigma\rho' \quad (16)$$

since it would not be expected that ρ and ρ' would be of the same value, or even sign. Such behavior is not noticed. Initial attack of $X^{\ominus}$ on R_2Hg seems unlikely for reasons already pointed out—the lack of effect of added $I^{\ominus}$ or H_2O. The only remaining possibility appears to be either electrophilic attack on carbon by some species with the Hg absorbing or blocking the effect of the substituent on the other ring, or a four-center system in which $\rho' << \rho$, perhaps because of the hybridization of mercury other than sp.[7]

Whether one pictures the transition state as in equation 15, or as

$$R-Hg-R \longrightarrow R-Hg-R \longrightarrow 2RHgX \quad (17)$$
$$X-Hg^{\oplus}X^{\ominus} \longleftarrow X-Hg^{\oplus}X^{\ominus}$$
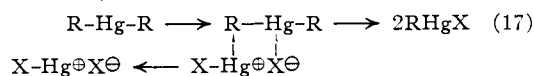
is probably immaterial, but the latter is consistent with the fact that the ease of ionization of the Hg–Z bond in HgZ_2 parallels the reactivity with R_2Hg compound, thus favoring ion pair attack over molecular attack.

CINCINNATI, OHIO

The Reduction of Amides to Amines *via* Nitriles by Lithium Aluminum Hydride[1]

BY MELVIN S. NEWMAN AND TADAMICHI FUKUNAGA[2]

The isolation of nitriles in lithium aluminum hydride reductions of amides indicates that part, if not all, of the reduction involves dehydration of amide to nitrile followed by reduction of nitrile to amine.

The reduction of unsubstituted amides to primary amines has often been accomplished by lithium aluminum hydride.[3] In discussion as to possible mechanisms for this type of reduction, attention has been directed to the nature of the complex hydride rather than to the organic moiety. With regard to the latter, it has been assumed that some species added to the carbonyl group as a first step.

(3) N. G. Gaylord. "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc.. New York. N. Y.. 1956. p. 544 ff.; also for stoichiometry of these reductions.

In an attempt to reduce triisopropylacetamide to 2,2,2-triisopropylethylamine an absorption band at 4.55 μ, indicative of nitrile, was noted in the crude product.[4] When the amide was treated with about one-half mole of lithium aluminum hydride, 55–66% yields of triisopropylacetonitrile were obtained, in addition to recovered amide. When excess reducing agent was used 2,2,2-triisopropylethylamine was obtained in almost quantitative yield from the corresponding nitrile.

To see whether reduction *via* the nitrile was due to the extreme steric hindrance in the amide, a similar experiment was carried out with benzamide.

(4) A band in the 4.5–4.6 μ region is characteristic for nitriles: L. J. Bellamy. "The Infrared Spectra of Complex Molecules." John Wiley and Sons. Inc., New York, N. Y.. 1958. p. 263.