

the infrared absorptions of the initial and the recovered hydrindanes were identical<sup>43</sup>). 8-Nitrohydrindane<sup>44</sup> was obtained after exhaustive treatment of the nitration product with methanolic sodium methoxide; b.p. 64–65° (0.6 mm.),  $n_D^{25}$  1.4875,  $d_4^{25}$  1.089,  $M_{RD}$  (calcd.) 45.11,  $M_{RD}$  (found) 44.61; major infrared absorption for C–NO<sub>2</sub> (6.54 and 7.37  $\mu$ ), and possibly *cis* ring<sup>42,43</sup> (11.77 and 12.42  $\mu$ ) structures, minor absorption for nitrite (5.85  $\mu$ ) and nitrate (6.10  $\mu$ ) groups. On the basis of their physical constants and absorption spectra, the 8-nitrohydrindanes obtained from *cis*- and from *trans*-hydrindanes are essentially identical.

**Conversion of 8-Nitrohydrindane to 8-Hydrindylamine.**—Samples of 8-nitrohydrindane from *cis*- and *trans*-hydrindanes were converted to 8-hydrindylamine by hydrogenation in ethyl ether over Raney nickel. The yields and physical properties of the crude reduction products are listed in Table III. The physical properties and the infrared spectra of the two products were practically the same; there was no absorption for nitro groups in the products.

Each reduction product was converted to N-8-hydrindylacetamide by reaction with excess acetic anhydride and sodium hydroxide. The crude products as derived from *cis*- and *trans*-hydrindanes were recrystallized from acetone as white crystals in 83 and 73% yields, respectively, of the properties listed in Table III. The N-8-hydrindylacetamides do not depress the melting

(44) The mixture of mononitrohydrindanes from nitration of *trans*-hydrindane, 8-nitrohydrindane and secondary nitro-*trans*-hydrindanes, absorbs at 11.77 and 12.42  $\mu$  (this absorption is similar to that exhibited by *cis*-hydrindane) and at 8.50 (strong) and 11.95  $\mu$  (this absorption is similar to that of *trans*-hydrindane). Upon removing the secondary nitro-*trans*-hydrindanes from the mixture by alkaline extraction, infrared absorption is no longer displayed at 8.50 and 11.95  $\mu$ .

TABLE III  
CONVERSIONS OF 8-NITROHYDRINDANE TO 8-HYDRINDYLAMINE AND TO N-8-HYDRINDYLACETAMIDE

Parent hydrindane <sup>a</sup>	8-Hydrindylamine <sup>b</sup>		N-8-Hydrindylacetamide	
	Yield, % <sup>c</sup>	$n_D^{25}$	Yield, % <sup>d</sup>	M.p., °C.
<i>cis</i> -	98.0	1.4923 <sup>e</sup>	83	88
<i>trans</i> -	98.5	1.4925 <sup>f,g</sup>	73	88

<sup>a</sup> Hydrocarbon nitrated to give 8-nitrohydrindane. <sup>b</sup> Lit.<sup>1</sup> (from reduction of 8-nitrohydrindane obtained from nitration of a commercial hydrindane)  $n_D^{20}$  1.4894. <sup>c</sup> Maximum yield of undistilled 8-hydrindylamine from hydrogenation of 8-nitrohydrindane. <sup>d</sup> Minimum over-all yield of pure N-8-hydrindylacetamide from 8-nitrohydrindane. <sup>e</sup>  $M_{RD}$  (calcd.) 42.83;  $M_{RD}$  (found) 42.79. <sup>f</sup>  $M_{RD}$  (found) 43.00. <sup>g</sup> See S. S. Nametkin, M. R. Rudenko and W. N. Gromova, *Chem. Abstr.*, **37**, 2367 (1943).

points of each other. It can be concluded that the tertiary nitration products from *cis*- and *trans*-hydrindanes are essentially similar.

*Anal.* Calcd. for C<sub>11</sub>H<sub>19</sub>NO: C, 72.93; H, 10.50; N, 7.73. Found: C, 72.97; H, 10.51; N, 7.64.

The similarity of the samples of crude 8-hydrindylamine was confirmed upon their conversion to N-8-hydrindylbenzamide, m.p. 97.5–98.0°, in excellent yields by reaction with benzoyl chloride and sodium hydroxide; the melting points of the derivatives were not depressed upon admixture.

*Anal.* Calcd. for C<sub>16</sub>H<sub>21</sub>NO: C, 79.01; H, 8.64; N, 5.76. Found: C, 79.16; H, 8.83; N, 5.80.

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

## Assisted Mechanistic Pathways in the Reactions of Organometallic Compounds

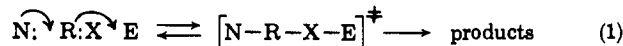
BY RAYMOND E. DESSY<sup>1</sup> AND FRANK E. PAULIK

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A consideration of the principles underlying the concept of nucleophilic assistance leads to the conclusion that such effects should be most readily observable in the reactions of organometallic compounds in solvents that are poor anion solvators. A model system is proposed, and the concept tested.

Although chemists have, for many years, tended strictly to compartmentalize reaction mechanisms into electrophilic and nucleophilic processes, there has been considerable attention drawn to the fact that some (or all) mechanistic pathways involve both electrophilic and nucleophilic participation.<sup>2</sup>

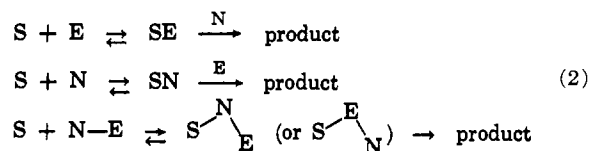
This is evidenced, for example, in the rates of solvolysis of a number of alkyl and aralkyl halides in a variety of solvents, which are correlated by the Swain equation,  $\log k/k_0 = ns_n + es_e$ , where  $n$  and  $e$  are the nucleophilicity and electrophilicity parameters of the solvent,  $s_n$  and  $s_e$  are sensitivity parameters dependent on the reaction type, and  $k$  and  $k_0$  are specific rate constants for the system, and reference system, respectively.<sup>3</sup> The mechanism involved has been represented pictorially by



The difficulties associated with the evaluation of the various parameters have been discussed by Gould,<sup>4</sup> but there seems little doubt that both E and N attacks are important in solvolytic reactions.

Bender<sup>5</sup> has pointed out that similar processes are certainly involved in the reaction of carboxylic acid derivatives, and he has described three broad classi-

fications of mechanistic pathways involving these compounds—electrophilic catalysis, nucleophilic catalysis and electrophilic–nucleophilic catalysis.



The word *assistance* might be applied to the actual effect of the so-called catalyst which is involved in the pre-rate-determining equilibrium, since in some cases this substance is not regenerated after the rate-determining process.

It is important to distinguish between complexing, or coordination, and assistance. Complexing, or coordination, focus on the process of replacement of ligand, by ligand. Assistance induces an increased reactivity in an adjacent part of a molecule by a coordination step, and it is this increased reactivity to which attention is drawn in this paper.

Electrophilic assistance has been found in solvolysis reactions of organic halides, Ag<sup>+</sup> and Hg<sup>2+</sup> serving as the electrophilic assistor, as well as solvent.<sup>6a,b</sup> In protic solvents it is often difficult to observe electrophilic assistance by added solute since few solutes are sufficiently more reactive to make up for differences in concentration between solute and solvent, and the latter serves as an often unseen electrophilic assistor.<sup>6c</sup>

(6) (a) I. Roberts and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 1063 (1937); (b) O. T. Benfey, *ibid.*, **70**, 2165 (1948); (c) C. G. Swain, *et al.*, *ibid.*, **72**, 4578 (1950); **74**, 2534 (1952); **74**, 2538 (1952).

(1) Alfred P. Sloan Fellow.

(2) For a discussion of the matter see J. Hine "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) C. G. Swain, *et al.*, *J. Am. Chem. Soc.*, **70**, 1119 (1948); **75**, 141 (1953); **77**, 3727, 3731 (1955).

(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt-Dryden, New York, N. Y., 1959.

(5) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

It is only in cases where the solvent is relatively ineffective in both its role of nucleophile and electrophile that electrophilic assistance by an added cation would be kinetically observable.

In a consideration of other specific solvent effects on electrophilic assistance, increased cation activity should be found with decrease in cation solvation, and Parker<sup>7</sup> has discussed the principles involved here. The fact that most kinetic investigations have employed dipolar protic solvents where the charge on the negative end of the dipole is highly localized, increasing its ability to solvate cation, has undoubtedly led to our lack of appreciable data in the area. Deuterium isotope effect studies, on acid catalysis, generally the most fruitful area for elucidating electrophilic assistance, is fraught with danger, as Bender has recently pointed out.<sup>8</sup>

A consideration of some of the fundamental principles concerning solvation which have been developed in recent years<sup>7</sup> makes it evident that *nucleophilic participation* can also be minimized by specific solvent interaction. Protic solvents strongly solvate anions through hydrogen bonding, thereby decreasing and leveling their activity ( $\text{Cl}^-$  vs.  $\text{Br}^-$  vs.  $\text{I}^-$ ) and potential importance as nucleophilic reagents. When a dipolar aprotic solvent is used, solvation of the anion is less appreciable (no hydrogen bonding) and activity is increased as well as over-all differentiation of anionic activity. This is exemplified by the strength of halogen acids in dipolar protic solvents as compared to aprotic dipolar solvents. Thus, since solvation of anions in protic solvents is greater the smaller the anion, and bond strengths are greater the smaller the anion, acid strengths are leveled. In dipolar aprotic solvents, the reverse is true and anion solvation assists dissociation of the acids with the most polarizable anion, and weakest H-X bond, to differentiate acid strength. A consideration of these concepts would lead to the conclusion that nucleophilic assistance would be most successfully sought and observable in aprotic or aprotic-polar solvents, such as dimethyl sulfoxide.

This is strongly evidenced by the fact that dimethyl sulfoxide aids remarkably the displacement reactions on carbon by nucleophiles.<sup>7,9</sup>

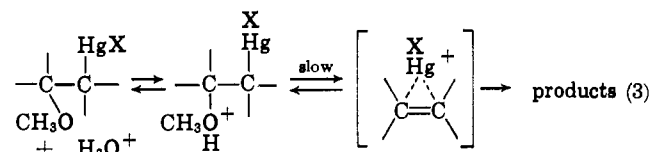
Just as electrophilic assistance is expected to be evident in systems containing available lone pairs of electrons near the reaction site, one would expect nucleophilic assistance to occur where electron deficiency was present near the attacked site. It is interesting that the best evidence for nucleophilic assistance at carbon is found in derivatives of carboxylic acids or carbonyl compounds where the carbon involved is electron deficient. The criteria of electron deficiency is met best, however, by organometallic compounds, where the metal is always electron deficient or potentially electron deficient (capable of expanding its octet).

One would hope therefore that in the properly chosen model organometallic system, kinetic evidence for nucleophilic assistance might be found.

In the cleavage of carbon-mercury bonds in various types of organomercury systems nucleophilic attack on mercury (assistance), in addition to the expected electrophilic attack on carbon, has been considered as a possible and significant interaction.<sup>10</sup> In some cases it has been looked upon only as an alternative due to the lack of actual proof. Once considered, the idea

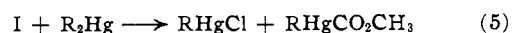
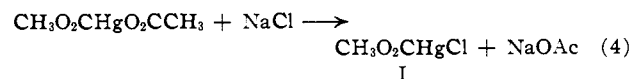
has often been discarded.<sup>11</sup> Furthermore, it is evident that specific solvent interaction minimized possible nucleophilic participation.<sup>12</sup> Dessy has suggested such nucleophilic assistance in the cleavages of carbon-mercury bonds by halogen acids. The data supporting this conclusion were massive, but nonetheless circumstantial.

With this in mind, and remembering the desire for direct kinetic evidence, it was decided to separate the attacked sites in the organometal. One possible system would be the oxymercuration products of olefins,  $\text{ROCH}_2\text{CH}_2\text{HgX}$ . Here the elements X and Y are separated by an ethylidene unit. Kreevoy<sup>13a</sup> has investigated the mechanism of deoxymercuration of these compounds by non-halogen acids, and proposed the mechanism



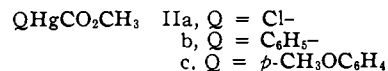
Unpublished observations by him<sup>13b</sup> suggest that in the halogen acid system, using HI, in protic solvents the reaction seems to have available three different routes, which involved kinetic expressions: (a) zero order in iodide, (b) first order in iodide, and (c) second order in iodide. Proton transfer is still not a part of the rate-determining process. Thus species such as  $\text{CH}_3\text{OCH}_2\text{---CH}_2\text{HgI}_2^-$  are indicated as *intermediates*, not transition states.

A series of compounds in which the attacked sites are somewhat closer together may be derived from the parent  $\text{CH}_3\text{O}_2\text{CH}_2\text{O}_2\text{CCH}_3$ .<sup>14</sup> Recent infrared and n.m.r. studies have shown these compounds to have the indicated structure.<sup>15</sup> By a series of interesting reactions

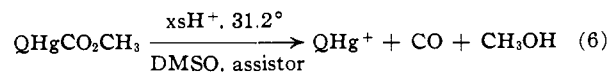


it is possible to prepare other related compounds which are members of a little-known class of organometallic compounds of the general formula,  $\text{R}_{n-1}\text{M}^n\text{CO}_2\text{R}'$ .<sup>16</sup>

The assisted acid decomposition of various members of this series, represented by formula II, has been



studied in dimethyl sulfoxide (DMSO) using a Van Slyke-Folch manometric apparatus to measure the amount of CO evolved as a function of time.



### Experimental

**Materials. Organomercurials.**—The synthetic methods for the preparation of the organomercurials used in this study may be found in reference 16.

(11) Cf. A. Corwin and M. A. Naylor, *ibid.*, **69**, 1004 (1947); E. Kaufman and A. H. Corwin, *ibid.*, **77**, 6280 (1955).

(12) O. W. Berg, W. P. Lay, A. Rodgmen and G. F. Wright, *Can. J. Chem.*, **36**, 358 (1958).

(13) (a) M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959); **82**, 739 (1960); (b) M. M. Kreevoy, personal communication.

(14) W. Scholler, W. Schrauth and O. W. Essers, *Ber.*, **46**, 2864 (1913).

(15) J. Halpern and S. F. A. Kettle, *Chem. Ind. (London)*, 668 (1961).

(16) For leading references to other members of this series and for the synthetic methods used, see F. E. Paulik and R. E. Dessy, *ibid.*, 1650 (1962).

(7) A. J. Parker, *Quart. Rev.*, **16**, 163 (1962).

(8) M. L. Bender, E. F. Pollack and M. Neveu, *J. Am. Chem. Soc.*, **84**, 595 (1962).

(9) Cf. L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).

(10) S. Winstein, T. G. Traylor and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955); S. Winstein and T. G. Traylor, *ibid.*, **77**, 3747 (1955); R. E. Dessy, G. Reynolds and J. Kim, *ibid.*, **81**, 2683 (1959); R. E. Dessy and J. Kim, *ibid.*, **83**, 1167 (1961).

**Alkali Metal Salts.**—All salts were commercially available reagent grade materials. The salts were dried to constant weight before use at temperatures between 150–200°.

**Phosphorus Compounds.**—The triphenylphosphine and triphenylphosphine oxide were obtained from Metal and Thermit Corporation, Rahway, N. J., and were purified by several recrystallizations from ethanol and benzene-petroleum ether, respectively.

**Liquids.**—The dimethyl sulfoxide (DMSO) employed was commercially available material purified by fractional distillation under vacuum, the middle fraction being retained.

The acetic acid employed was reagent grade material purified by fractional distillation from potassium permanganate, drying the middle fraction over magnesium perchlorate, and again fractionally distilling the material, retaining the middle fraction. The refractive index of the final product at 25° was 1.3699 (lit. 1.36976).

The phenylmercaptan and phenol used were reagent grade materials purified by fractional distillation. Concentrated reagent grade HCl was used as received, and anhydrous HCl was passed through Drierite columns before use.

**Kinetic Apparatus.**—A Van Slyke-Folch manometric apparatus was used to measure gas evolution at constant volume. The reaction vessel was a 100-ml. flat-bottomed flask equipped with a side arm and a stopcock fitted with a rubber septum through which the final reactant (acetic acid) was injected by means of a hypodermic syringe. A magnetic stirrer was used.

The temperature regulating system consisted of a water bath under constant agitation in which a bimetallic thermo-regulator and a heating unit were immersed. Water from the bath was circulated through the gas chamber jacket and around the reaction vessel by means of a centrifugal circulating pump. Temperature control was within  $\pm 0.075^\circ$ .

**Typical Treatment of Rate Data.**—Second-order rate constants were calculated from the equations

$$k_2 = 2.303/t(b - 3a) \times \log(b - 3x)/(a - x), \text{ or (I)}$$

$$k_2 = 2.303/t(b - a) \times \log a(b - x)/b(a - x) \text{ (II)}$$

In these equations  $a$  corresponds to the initial concentration of mercury compound,  $b$  to the initial concentration of halide ion and  $x$  to the amounts of mercury compound reacted, as determined by the quantity of carbon monoxide evolved. Equation I was employed when two halide ions were used in a post-rate-determining step, while equation II was employed when only one halide ion was necessary for the stoichiometric reaction. Plots of  $t$  vs.  $\log(b - 3x)/(a - x)$  or  $\log(b - x)/(a - x)$ , respectively, gave straight lines with slopes of  $2.303/k_2(b - 3a)$  or  $2.303/k_2(b - a)$ . The third-order rate constants were obtained by dividing  $k_2$  by the concentration of acetic acid, which was present in a large excess.

Taking run 9 as a sample the data were obtained as follows; to a mixture of 10 ml. of 1 *M* LiCl and 10 ml. of 0.2 *M* carbomethoxymercuric chloride contained in an equilibrated, thermostated Van Slyke reaction vessel was added 10 ml. of 4.0 *M* acetic acid. Gas evolution began immediately, giving the following raw experimental data and calculated concentration terms. The pressure difference corresponding to 100% reaction was calculated from the gas law, the known free volume of the apparatus, the number of moles of carbomethoxymercurial, and the thermostating temperature. Where concentration ratios are employed in the rate equation, pressure difference terms may be substituted, as indicated. Duplicate runs were made in all cases, and average values of the rate constants are reported in the table. The precision was  $\pm 3\%$ .

Run 9				
Time, min.	Pressure, cm.	$x$ , (P - P <sub>0</sub> )	$a - x$ (Hg)	$b - 3x$ (Cl <sup>-</sup> )
0	15.0	0	39.8	199
1.2	15.8	0.8	39.0	196.6
3.8	20.0	5.0	34.8	184.0
6.8	24.1	9.1	30.7	171.7
11.1	28.5	13.5	26.3	158.5
15.2	32.0	17.0	22.8	148.0
23.2	37.0	22.0	17.8	133.0
34.8	42.0	27.0	12.8	118.0
44.1	44.7	29.7	10.1	109.9
51.7	46.4	31.4	8.4	104.8

Data from run 6 indicate, for all practical purposes, that CO is insoluble in DMSO. In this experiment the calculated pressure difference was 30.1 cm. and the observed value was 30.2, indicating that any correction for solubility of CO in DMSO is not important.

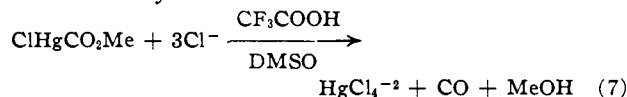
### Discussion

Initial attempts indicated that decomposition induced by acetic (run 1) or trifluoroacetic acid (run 2)

was slow (Table I), while hydrochloric acid (run 3) resulted in rapid decomposition.

The rapid reaction with HCl vs. the slow reaction with CF<sub>3</sub>CO<sub>2</sub>H, both very strong acids, suggested that anion assistance might be important.

The addition of equivalent amounts of chloride ion to run 2 (run 4) led to the rapid evolution of one-third of the expected amount of CO. Further additions of two more equivalents of chloride ion finally led to complete CO evolution (runs 5, 6). This suggests a stoichiometry



The addition of HgCl<sub>2</sub> to this reaction resulted in a decreased rate of evolution of CO because of the competition for Cl<sup>-</sup> by ClHgCO<sub>2</sub>Me and HgCl<sub>2</sub> as might be expected.

The reaction of acetic acid with carbomethoxymercuric chloride in the presence of LiCl led to an evolution of CO which followed the rate law

$$\frac{dx}{dt} = \frac{d(\text{CO})}{dt} = k(\text{"Hg"} - x)(\text{HOAc} - x)(\text{Cl}^- - 3x) \quad (8)$$

"Hg" = carbomethoxymercury derivative

which is in agreement with the stoichiometry of eq. 7 (runs 7–11).

The rate law was examined over Cl<sup>-</sup>/"Hg" mole ratios of 3:1, 4:1, 5:1 and 5.9:1 and the  $k_3$ 's obtained all fall within the range  $1.48\text{--}1.64 \times 10^{-3} \text{ l.}^2/\text{mole}^2 \text{ sec.}$  (runs 7a, 8, 9, 10). A small salt effect exists as indicated by run 7b.

When the rate law was examined over "Hg"/HOAc mole ratios of 1:10 and 1:20, the  $k_3$ 's obtained differed by approximately 35%, the difference being attributed to the appreciable change in solvent properties in these two systems (runs 9, 11).

The decomposition of phenylcarbomethoxymercury and *p*-methoxyphenylcarbomethoxymercury by HOAc/LiCl system also obeys the rate law given by eq. 8 as expected (runs 12, 13). The fact that there is little difference in all three rates suggests that the second group on mercury has little effect on the rate and course of reaction.

In an attempt to elucidate the possible function of the assistor in these processes, other anionic, molecular or intramolecular (incorporated in the attacking acid) ligands for mercury were tested for assistor activity (runs 14–21). It should be noted that in the case of bromide or iodide, the rate expression followed was

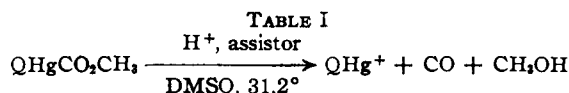
$$dx/dt = d(\text{CO})/dt = k(\text{"Hg"} - x)(\text{HOAc} - x)(Y - x) \quad (9)$$

(Y = Br<sup>-</sup> or I<sup>-</sup>)

This would suggest that under these conditions phenylmercuric halide forms a complex with chloride ion (C<sub>6</sub>H<sub>5</sub>HgCl<sub>3</sub><sup>-</sup>), but it does not do so with bromide or iodide ion. This is consistent with the fact that metal-halogen bond strengths decrease in the order, Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>. In aqueous solution the iodide ion is a better coördinator to mercury, as compared to chloride ion, but this is because of the higher energy of hydration of the chloride ion which results in a lesser tendency for it to become involved in complex formation.<sup>17</sup> In dimethyl sulfoxide, a poor solvating agent for anions, the normal sequence is to be expected.<sup>7</sup> It is surprising, though, that the break is so clean between chloride ion and bromide ion.

The previously mentioned change in rate law in going from Cl<sup>-</sup> to Br<sup>-</sup> or I<sup>-</sup> is real as shown by runs 15

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 180.



Run	Substrate	Concn., mole/l.	Acid	Concn., mole/l.	Assistor	Concn., mole/l.	$k_2$ , l. <sup>2</sup> /mole <sup>2</sup> sec. × 10 <sup>4</sup>
1	ClHgCO <sub>2</sub> CH <sub>3</sub>	0.067	HOAc	1.33	...	...	No reactn.
2	ClHgCO <sub>2</sub> CH <sub>3</sub>	.125	CF <sub>3</sub> CO <sub>2</sub> H	0.125	...	...	Too slow
3	ClHgCO <sub>2</sub> CH <sub>3</sub>	.125	HCl	.125	(HCl)	...	Too fast
4	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	CF <sub>3</sub> CO <sub>2</sub> H	.067	LiCl	0.067	1/3 CO
5	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	CF <sub>3</sub> CO <sub>2</sub> H	.067	LiCl	.133	2/3 CO
6	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	CF <sub>3</sub> CO <sub>2</sub> H	.067	LiCl	.200	All CO
7a	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	LiCl	.200	1.37
7b <sup>a</sup>	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	LiCl	.200	1.54
					LiClO <sub>4</sub>	.133	
8	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	LiCl	.267	1.56
9	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	LiCl	.333	1.64
10	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	LiCl	.393	1.48
11	ClHgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	0.67	LiCl	.333	2.01
12	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	LiCl	.333	0.57
13	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.050	HOAc	1.00	LiCl	.250	0.56
14	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.050	HOAc	0.67	LiBr	.150	3.88
15	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	.67	NaBr	.067	4.43
16	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.050	HOAc	.67	NaI	.100	38.6
17	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	.067	No reactn.
18	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.067	HOAc	1.33	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PO	.067	Too slow
19	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.100	C <sub>6</sub> H <sub>5</sub> OH	0.10	(C <sub>6</sub> H <sub>5</sub> OH)	...	No reactn.
20	C <sub>6</sub> H <sub>5</sub> HgCO <sub>2</sub> CH <sub>3</sub>	.100	C <sub>6</sub> H <sub>5</sub> SH	0.10	(C <sub>6</sub> H <sub>5</sub> SH)	...	Too fast
21	ClHgCO <sub>2</sub> CH <sub>3</sub>	.100	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CO <sub>2</sub> H	1.00	(C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CO <sub>2</sub> H)	...	No reactn.

<sup>a</sup> Only a single run was made; all other measurable runs were made at least in duplicate.

and 16 which have "Hg"/Br<sup>-</sup> and "Hg"/I<sup>-</sup> mole ratios of 1:1 and 1:2. These runs were followed to 75 and 90% completion, respectively, without significant deviation from the rate law.

The reactions involving other assistors were either too fast or too slow to follow kinetically under the conditions used; however, from such observations one may order the various assistors, RSH > I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P → 0 > (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P, C<sub>6</sub>H<sub>5</sub>OH.

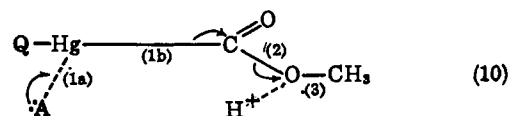
It is readily apparent that the ligand to mercury has three possible interactions with the metal: (a) bonding *via* donation from a ligand lone-pair to an empty sp<sup>x</sup> hybrid orbital of mercury previously occupied by solvent, (b) d<sub>π</sub>-d<sub>π</sub> back-bonding involving a 5d<sup>10</sup>-orbital of mercury and an empty d of the ligand, and (c) antibonding involving a filled p-(or sp<sup>x</sup>-hybrid) orbital of the ligand and an empty p-(or sp<sup>x</sup>-hybrid) orbital of mercury.<sup>18</sup> The latter is equivalent in end result to polarization interactions.

An examination of the known properties of the assistors used reveals that oxygen-mercury bonds are notoriously weak while sulfur-mercury or halogen-mercury bonds are stronger. Phenol is a poor assistor while thiophenol<sup>19</sup> or the halogens are excellent assistors (runs 14-16, 20). There seems to be no direct relationship between base strength and assisting ability. The fact that phosphorus in triphenylphosphine does not serve as an assistor (run 17) but that oxygen in triphenylphosphine oxide does (run 18) is indicative of the importance of π-antibonding or polarizability (c) as compared to d<sub>π</sub>-d<sub>π</sub> back-bonding (b). One might empirically conclude then that at least 2 lone-pairs are necessary for assistance in this case. We can picture such assistance as follows, with the bonding processes labeled 1-3.

The timing of the processes 1-3 is delineated and the concept of assistance is strengthened by an examination of runs 7-11. The production of Li<sup>+</sup>, OAc<sup>-</sup> is

(18) L. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 37.

(19) Fresh solutions of thiophenol in DMSO led to reactions too fast to measure. Kinetics in the system were further complicated by the oxidation of thiophenol to diphenyl disulfide by the DMSO.



to be noted, and a consideration of the work of Kolthoff and Reddy<sup>20</sup> suggests that ion pair formation will not be excessive. If step 3 occurred in a pre-rate-determining equilibrium, then the observed rate law (eq. 8) should not be obeyed. Since sulfide-, halide- and amine-mercury complexes are known and isolable,<sup>21</sup> it seems likely that step 1a occurs before 2, 3.

In the case of the thiophenol, where the assistor and proton are in the same molecule and attached to one another, the increased availability of the proton as a result of process 1a is to be noted. In this case it is logical to consider an assisted five-center mechanism.

Geometry is probably important in determining whether multi-center assisted pathways occur, since although preliminary observations indicate that thio-urea assists the attack of acetic acid and run 20 shows rapid reaction with thiophenol, phenylthioacetic acid is unreactive (run 21).

As has been described above, the function of process 1a can be conceptually divided into several phases, the most important of which appears to be π-antibonding which gives rise to 1b; the latter could also be the result of induced polarization by the assistor; this results in increased freedom of the CO<sub>2</sub>Me grouping and therefore increased electron density on the methoxyl oxygen. Attack by proton is thereby facilitated, or *assisted* by the ligand attached to mercury.

An examination of the spectra of a large number of inorganic complexes containing various central metal atoms and various ligands enables the ligands to be

(20) I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962).

(21) (a) W. E. Parham and J. M. Wilbut, *J. Am. Chem. Soc.*, **81**, 607 (1959); (b) S. F. Birch, R. A. Dean and W. J. Hunter, *J. Org. Chem.*, **23**, 1026 (1958); (c) A. A. Schilte and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959); (d) D. Leaver and F. Challenger, *J. Chem. Soc.*, 39 (1957); (e) D. Kosyegi and E. Salgo, *Z. Anal. Chem.*, **136**, 411 (1952); (f) Davies and L. H. Thomas, *J. Chem. Soc.*, 1446 (1947); (g) W. J. Lile and R. C. Menzies, *ibid.*, 617 (1950).

arranged in a series according to their ability to cause d-orbital splitting. This is the so-called spectrochemical series and is the sequence that should be obeyed when metal-ligand interaction is largely electrostatic in origin (crystal field theory). In part, this series is  $I^- < Br^- < Cl^- < (C_6H_5)_3PO$ . Where the mixing of metal atom orbitals with ligand atom orbitals becomes important, d-electron cloud expansion also must be considered. The relative effect of ligands in expanding the d-electron cloud has been named the nephelauxetic (cloud expanding) series which is, in part,  $(C_6H_5)_3PO < Cl^- < Br^- < I^-$ .<sup>22,23</sup> The relationship between this series and assistor activity is apparent. The nephelauxetic effect has also been correlated with the polarizability or covalency of the ligands.<sup>24</sup> One could visualize such d-orbital expansion in the present case as resulting from  $\pi$ -antibonding which will increase the charge on the metal atom. Such an effect could also result from the donation of charge to the metal atom by the polarization of the assistor since the observed series of increasing assistor activity does parallel the increasing polarizability and decreasing ionization potential of the series of ligands considered. The result of increased charge on the metal atom is to weaken the M-C bond; the basic arguments involved are to be found in discussions of polarization theory and the so-called *trans* effect. In summary, whatever the source, the effect of covalency is to delocalize (render more diffuse) the electronic distribution around the metal atom and to weaken the carbon-metal bond.

Evidence for this weakening of M-C bonds by coordination has been cited by Brownstein, *et al.*,<sup>25</sup> who were able to correlate the nuclear magnetic resonance frequencies of the methyl and methylene hydrogens in triethylaluminum and triethylgallium with the ability of solvent to coordinate with the electron-deficient metal. Increased electron density about the metal atom resulted in a decreased tendency to share electrons in an M-C bond.

The concept of assistance may be a fairly general

(22) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 593.

(23) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

(24) D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(25) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, *J. Am. Chem. Soc.*, **81**, 3826 (1959).

phenomenon, since work in these laboratories indicates that the reaction of tributyltin hydride with acetic acid is assisted by halide ion.

The concept also explains a number of facts concerning organometal reactions. For example, it appears that in many organometallic compounds the rate of cleavage of the metal-carbon or metal-hydrogen linkages is not a function of the acidity of the acid used alone but is also related to the ability of the atom to which the hydrogen is attached to coordinate with a metal atom. Coates and Huck<sup>26</sup> have reported that the rates of cleavage of dimethylberyllium by active hydrogen compounds is in the order  $ROH > R_2NH > RSH$ . Organoboron compounds react more rapidly with carboxylic acids than the halogen acids.<sup>27</sup>

The rate of reaction of  $LiBH_4$  with HA increases along the series  $C_6H_6, C_4H_5N, t-BuOH, CH_3OH$ , as HA is varied, while the  $K_a$ 's of the acids increase along the series  $C_4H_5N, t-BuOH, CH_3OH, C_6H_6$ .<sup>28</sup>

Finally, Coates has introduced a nearly identical concept to explain the different orientations of cleavage in the reactions  $C_6F_5HgR + HCl \rightarrow$ , and  $C_6F_5HgR + Br_2 \rightarrow$ .<sup>29</sup>

The practical applications of this concept of assistance seem very evident. It should be possible to increase the ability of an organometal to donate a carbanion to a substrate or increase the ability of a metal hydride to donate a hydride ion to a substrate. Finally it is felt that this investigation points out the advantages to be gained by the application of the basic philosophies and nomenclature of the inorganic chemist to the field of reaction mechanisms involving organometallic compounds. A review of the area has been presented by Dessy and Paulik.<sup>30</sup>

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(26) G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4512 (1952).

(27) H. C. Brown in "Organometallic Chemistry," Edited by H. Zeiss, ACS Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, p. 111.

(28) R. E. Dessy and E. Grannen, Jr., *J. Am. Chem. Soc.*, **83**, 3953 (1961).

(29) R. D. Chambers, G. E. Coates, J. G. Livingstone and W. K. R. Musgrave, *J. Chem. Soc.*, 4367 (1962).

(30) R. E. Dessy and F. E. Paulik, *J. Chem. Educ.*, **40**, 185 (1963).

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## Basicity of N-Nitrosamines. II.<sup>1</sup> Aqueous Sulfuric Acid Solutions<sup>2,3</sup>

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The ultraviolet spectra of dimethyl-N-nitrosamine and diisopropyl-N-nitrosamine were examined in aqueous sulfuric acid solutions and the changes of spectra were observed at a number of acid concentrations. The changes of spectra indicate the N-nitrosamine molecule exists in four spectroscopically distinguishable forms in aqueous acidic solution, with the proportion of each determined by the acid concentration. The first and second equilibrium constants were calculated, and their dependence on acid concentration indicates the reactions producing spectral change are the formation of hydrogen bonds between the N-nitrosamine molecule and sulfuric acid. White, crystalline 1:1 addition compounds of di-n-heptyl-N-nitrosamine, di-n-octyl-N-nitrosamine and bis-(2-ethylhexyl)-N-nitrosamine with perchloric acid were prepared.

In an attempt to measure the base strengths of a series of N-nitrosamines, we have measured the spectra

(1) Part I: *J. Am. Chem. Soc.*, **85**, 435 (1963).

(2) This work was supported by the Office of Ordnance Research, U. S. Army.

(3) Taken in part from the Ph.D. Thesis of W. S. L., University of Cincinnati, 1961.

of such compounds in a series of solutions in aqueous sulfuric acid. Rather than finding the expected simple change due to an acid-base reaction, we observed a complicated series of changes. These complications are reminiscent of the sensitivity of the spectra of N-nitroso compounds to solvents, previously observed by Haszel-