Organometallic Electrochemistry. II. Carbanion Stabilities

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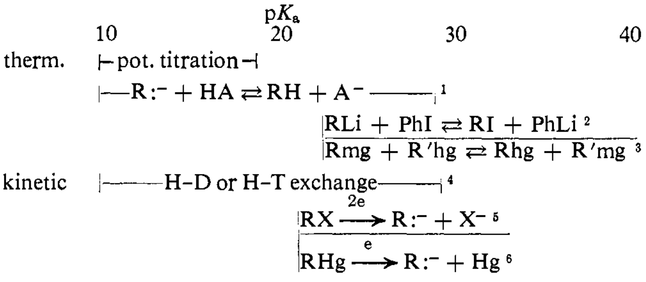
Abstract: Equilibrium constants (K_{ex}) for the process Rmg + Phhg $\rightleftharpoons$ Rhg + Phmg have been calculated from data derived from n.m.r. spectra of $R_2Mg + R_2Hg \rightleftharpoons$ systems. There is an excellent correlation between these data and the similar values reported by Applequist for the RLi + PhI $\rightleftharpoons$ RI + PhLi system. It would appear that the relative K values represent the nucleus for a primitive sequence of carbanion stabilities arrived at by measurements involving thermodynamic control. Such a sequence relates directly to a series of pK_a values for the parent weak acids, RH. A correlation between the $E_{1/2}$ value for the process $RHg \xrightarrow[e]{} R:^- + Hg$ and log K_{ex}, and thus pK_a, is shown in the region of parent acid pK_a values of 35–40. This correlation may prove a useful tool in establishing relative carbanion stabilities or hydrocarbon acidities, and may have some quantitative value.

The concept of carbanion stability, and the concomitant parent hydrocarbon acidity, has, as the following equation implies, both a thermodynamic and

$$R:^- + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RH + A:^- \qquad (1)$$

kinetic aspect. Attempts at establishing a quantitative relationship among a series of organic radicals have been made by both approaches. It is immediately evident that high exchange rates at low pK_a values, and the poor reliability and low availability of pK_a data at the high end of the scale make a comparison of the two approaches difficult. Cram has excellently and definitively reviewed this area.[7] The conclusion is that in the range of pK_a values from 4–20 the correlation between kinetic and thermodynamic parameters is poor. Beyond 20, when the reference acid–base pair is so constituted that the proton donor is a much stronger acid than the carbon acid generated, and k_{-1} can approach diffusion control values, there is reason to expect a correlation, and limited data would suggest that this expectation is realized. However, such comparisons are weakest, and often nonexistant in the critical range of pK_a = 30–40.



As the chart indicates, Applequist[2] has probed thermodynamically the region occupied by simple derivatives of sp^3 and sp^2 carbon, employing as his tools the evaluation of the position of equilibrium in a metal–halogen exchange system (eq. 2). Simultaneously,[3] preliminary work in this laboratory derived similar information from a system in which metal–metal interchange was involved (eq. 3).

$$RLi + PhI \overset{K}{\rightleftharpoons} RI + PhI \qquad (2)$$

$$Rmg + R'hg \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} Rhg + R'mg \qquad (3)$$

The basic concept in each approach has been the feeling that at equilibrium the most stable incipient carbanion would prefer to be paired to the most electropositive element. The metal–metal exchange system has the attribute of avoiding possible complications due to Wurtz coupling, and dehydrohalogenations, side reactions which seriously interfere with unlimited extension of the halogen–metal interchange approach. It is one purpose of this paper to (a) present the data currently accumulated from observations on equilibrium 3 concerning K, and k_2, k_{-2}, (b) compare these with similar data derived from system 2, and (c) in light of these correlations discuss carbanion stabilities and their hydrocarbon acidities in the range from 30–40.

While this manuscript was being prepared, Streitwieser reported on the attempted correlation of the polarographic half-wave potentials for reduction of RX compounds, and the acidity of the corresponding hydrocarbons, RH.

$$\begin{array}{ll} RX + e \longrightarrow R\cdot + X^- & RHgX + e \longrightarrow RHg + X^- \\ R\cdot + e \longrightarrow R:^- & RHg + e \longrightarrow R:^- + Hg \qquad (4) \\ RX + 2e \longrightarrow R:^- + X^- & \\ \text{a} & \text{b} \end{array}$$

The polarographic reductions of the halides (eq. 4a) were electrochemically irreversible, and the half-wave potentials do not have simple thermodynamic significance since they are related directly to a rate process at the electrode. The process giving rise to this potential appeared to involve radical intermediates, as

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(1) (a) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932); (b) W. K. McEwen, *ibid.*, **58**, 1124 (1936); (c) C. H. Langford and R. H. Burwell, *ibid.*, **82**, 1503 (1960); (d) A. Streitwieser and J. I. Brauman, *ibid.*, **85**, 2633 (1963).

(2) (a) D. E. Applequist and P. F. O'Brien, *ibid.*, **85**, 743 (1963); (b) J. Eastman, personal communication.

(3) R. E. Dessy and R. M. Salinger, *Tetrahedron Letters*, 729 (1963).

(4) (a) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); (b) R. E. Dessy, Y. Okazumi, and A. Chen, *ibid.*, **84**, 2899 (1962); (c) A. I. Shatenshtein in "Advances in Physical-Organic Chemistry," Vol. I, Academic Press Inc., New York, N. Y., 1963; (d) A. Streitwieser, W. C. Langworthy, and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 1761 (1963); (e) A. Streitwieser, R. A. Caldwell, and M. R. Granger, *ibid.*, **86**, 3578 (1964).

(5) A. Streitwieser and C. Perrin, *ibid.*, **86**, 4958 (1964).

(6) Present work.

(7) D. J. Cram, "Fundamentals of Carbanion Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

evidenced by the low value of αn_a (the product of the transfer coefficient and the number of electrons transferred in the rate-determining process), and the lack of correlation of the potentials with σ in a Hammett plot.

It is known[8] that in aqueous solutions reduction of RHgX compounds involves two one-electron steps, the first an electrochemically reversible step giving the subvalent species RHg,[9] the second an irreversible step yielding the carbanion (eq. 4b). Jensen[10] has pointed out that the species $\mathrm{RHg^+}$ is a remarkably pure source of unsolvated carbonium ion. The bulk of mercury shields the incipient carbonium ion from solvation. Equally of value, it would appear, is that specific R–Hg interactions are limited to inductive and polarization phenomena because of the poor orbital overlap encountered in an interaction requiring π bonding. For this reason, the potentials at which $\mathrm{RHg} \xrightarrow{e} \mathrm{R{:}^-} + \mathrm{Hg}$ should have some correlation with carbanion stabilities. It is the further purpose of this paper to present data bearing on the nature of RHg, and to compare this kinetically determined parameter with the thermodynamic sequences mentioned.

Results and Discussion

Redistribution Processes. In organometallic chemistry, redistribution reactions have come, through the well-executed original work of Calingaert, *et al.*,[11] to mean distribution or exchange equilibria such as

$$\mathrm{Rm} + \mathrm{Qm'} \underset{K}{\rightleftharpoons} \mathrm{Rm'} + \mathrm{Qm}$$

$$(\mathrm{Q} = \mathrm{R}, \mathrm{R'}, \mathrm{X}, \mathrm{OR}, \mathrm{H};\ \mathrm{R} = \mathrm{R})$$

The symbol m represents a metal, M, and a less than normal number of valence positions.

There is much to be gained from considering R and Q as ligands to the metal, and this form will be followed in the discussion below.

Calingaert's original work, although referring to many systems where Q = X, really reported data from which K could be determined for systems where Q = R′ and m = m′, and few for m ≠ m. In such cases, using Lewis acid catalysts, what was termed statistical distribution within a family of organometallics was noted. It is a relatively easy matter to analyze the parameters that must be controlled within definite limits to give such distribution. Since the nomenclature will be useful in the following discussion, a view of these factors, employing the notation of Leffler and Grunwald[12] follows. Alternatively, the views and data of Van Wazer[13] in this area may be used.

The standard free energy of an organometallic compound $\mathrm{Q}_{n-1}\mathrm{MR}$ may be noted, separating the bond of interest, R–m, from the substituent zone, $\mathrm{Q}_{n-1}\mathrm{M}-$, and assuming additivity where I is an interaction term,

$$\bar{F}^\circ = F_{\mathrm{Q}_{n-1}\mathrm{M}-} + F_{\mathrm{Rm}} + I_{\mathrm{Q}_{n-1}\mathrm{M}-,\mathrm{Rm}}$$

F values are independent additive terms, and n is the normal valence of M. I is factorable

$$I_{\mathrm{Q}_{n-1}\mathrm{M}-,\mathrm{Rm}} = I_{\mathrm{Q}_{n-1}\mathrm{M}-}I_{\mathrm{Rm}}$$

If $I = 0$, and translational and rotational entropy contributions are negligible, then what may be termed statistical distribution of the groups will be observed, and the external symmetry numbers of the molecules involved may be used to calculate K. For example

$$\begin{array}{cccc} & \mathrm{R_4Sn} + \mathrm{SnR'_4} & \overset{K}{\rightleftharpoons} & \mathrm{2R_2SnR'_2} \\ \sigma & 12 \qquad 12 & & 2 \end{array}$$

$$\Delta S^\circ = R \ln \frac{(12)^2}{(2)^2} = 7.11 \text{ units}$$

$$K_{\mathrm{calcd}} = 36, \qquad K_{\mathrm{found}} = 37^{14}$$

It appears important to emphasize that despite the feelings that have been generated by Calingaert's original work in the $\mathrm{R_4Sn/R'_4Sn}$, $\mathrm{R_4Pb/R'_4Pb}$, $\mathrm{R_2Hg/R'_4Pb}$ areas, where random distribution was observed within a given metal system, many cases of nonrandom distribution occur in the literature, particularly where R, X/M or R, OR/M distributions are involved.

Even in R, R, M distributions, nonrandomness occurs

$$\mathrm{(CH_3)_2Hg} + \mathrm{(C_6H_5)_2Hg} \rightleftharpoons \mathrm{2CH_3HgC_6H_5} \quad K = 4^{15a}$$

but

$$\mathrm{(CH_8)_2Hg} + \mathrm{(C_6F_5)_2Hg} \longrightarrow \mathrm{2CH_3HgC_6F_5} \quad K = \infty^{15b}$$

and

$$\mathrm{(CH_3)_2Hg} + \mathrm{(C_6H_5CH_2)_2Hg} \rightleftharpoons \mathrm{2CH_3HgCH_2C_6H_5} \text{ nonrandom}^{15c}$$

when M ≠ M′

$$\mathrm{Ral} + \mathrm{R'b} \rightleftharpoons \mathrm{R'al} + \mathrm{Rb} \quad \text{nonrandom}^{16a}$$

$$\mathrm{Rhg} + \mathrm{R'pb} \rightleftharpoons \mathrm{R'hg} + \mathrm{Rpb} \quad \text{nonrandom}^{16b}$$

This suggests that Calingaert's *statistical* distribution data are necessarily derived from systems where the ligands involved do not differ markedly in electronegativity, steric requirements, or resonance interaction capabilities, because I will be affected by the following factors: (a) the effect of Q on the effective charge, and hybridization of M, (b) resonance interaction between M and Q and/or R, and (c) nonbonding effects such as steric hindrance and dipole interactions. These effects are very difficult to evaluate in totality at the present, although the qualitative effect of each individually can often be predicted from fundamental principles. For example, as one proceeds from $\mathrm{R_4M}$ to $\mathrm{MX_4}$, the s character in the orbital extended toward R should increase, strengthening the R–m bond, as the positive charge on M increases.[17] In group III derived materials, interaction of the $\mathrm{C_6H_5MX}$ system should be considered because of the availability of the empty p orbital on M.[18] Finally, in the upper portions of the table, steric proximity effects may alter possible resonance interactions, distort the σ framework,

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[8] N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 35 (1963).

[9] B. Gowenlock, *J. Chem. Soc.*, 535 (1958).

[10] F. R. Jensen, L. D. Whipple, D. K. Wedegaerther, and J. A. Landgrebe, *J. Am. Chem. Soc.*, **82**, 2446 (1960).

[11] G. Calingaert, *et al.*, *ibid.*, **62**, 1099, 1107 (1940).

[12] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

[13] J. R. Van Wazer, *et al.*, *J. Am. Chem. Soc.*, **86**, 802, 807, 811, 814 (1964).

[14] *Cf.* A. E. Stearn, *ibid.*, **62**, 1630 (1940).

[15] (a) M. D. Rausch, Symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 12–15, 1963; (b) G. E. Coates, *J. Chem. Soc.*, 4367 (1962); (c) G. F. Wright, private communication.

[16] (a) R. Wooster, *Ann.*, **629**, 89 (1960); (b) G. Calingaert, H. Soroos, and H. Shapiro, *J. Am. Chem. Soc.*, **63**, 947 (1941).

[17] For a discussion of n.m.r. studies in this area, *cf.* N. Flitcroft and H. D. Kaesz, *ibid.*, **85**, 1377 (1963).

[18] For evidence of C=C=b interaction, *cf.* T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

or allow dipole interactions.[19] Specific solvent interactions may affect the free energy of one component of a system enough to allow complete conversion of the system members to this form.

Considering only (a), and viewing ligands R and Q competing for sights on m and m′, the most electronegative or stable ligands should, at equilibrium, lie attached to the most electropositive central unit.

For the three types of exchange processes known this seems to be an experimentally confirmed statement, and the evidence has been reviewed.[20] Of specific

$$\mathrm{Rm} + \mathrm{Rm} \overset{K}{\rightleftharpoons} \text{type I}$$

$$\mathrm{Rm} + \mathrm{Qm} \rightleftharpoons \text{type II}$$

$$\mathrm{Rm} + \mathrm{m} \rightleftharpoons \text{type III}$$

interest to a study of carbanion stabilities *via* determination of K is a system in which an organic radical exists before exchange in a condition where it has no incipient ionic character, or slight carbanionic character, and after exchange exists in an environment in which high negative charge localization is present in the group. Type III involves heterogeneous systems, and type II, for most metals, involves structural problems. Type I meets the basic requirements.

Because the structure of RLi compounds is complex, and often unknown, and group III derivatives pose the problem of unsymmetrical species, $RR_2'M$, it was decided to investigate group II–group II interchanges. In donor solvents, such as THF or ether, where R is methyl, preexchange R–m life times are too short (1 msec. or less) for Mg–Zn, Mg–Cd, or Zn–Cd pairs.[21] Only the Mg–Hg system permits simultaneous kinetic and thermodynamic studies.

N.m.r. data, based on chemical-shift information, indicate also that CH_3 groups attached to Hg have little carbanionic character, their proton resonance lying considerably downfield from the corresponding group attached to Cd, Zn, or Mg.[21]

Equilibrium Data. For this reason an investigation of the equilibria

$$R_2Mg + R_2'Hg \rightleftharpoons R_2'Mg + R_2Hg$$

via n.m.r. spectroscopy was undertaken. In only one case (C_6H_5, CH_3) was evidence of unsymmetrical species, RHgR′, discernible. N.m.r. does not reveal any information concerning the existence, or lack of existence, of RMgR′. For these reasons equilibrium constants were calculated on the basis of K = (R′mg)(Rhg)/(Rmg)(R′hg). Paired triad experiments were performed where possible to confirm that the following was true. All experiments were conducted at approx-

$$\mathrm{Rmg} + \mathrm{R'hg} \rightleftharpoons \mathrm{Rhg} + \mathrm{R'mg} \quad K_1$$

$$\mathrm{R'mg} + \mathrm{R''hg} \rightleftharpoons \mathrm{R'hg} + \mathrm{R''mg} \quad K_2$$

$$\mathrm{Rmg} + \mathrm{R''hg} \rightleftharpoons \mathrm{Rhg} + \mathrm{R''mg} \quad K_3 = K_1K_2$$

imately 0.5 M concentrations in glyme at 33°.

Table I shows the results obtained, where equilibrium constants are reported normalized to C_6H_5.

Table I

R	Log K Rmg + C_6H_5hg glyme $\uparrow\downarrow$ 33° C_6H_5mg + Rhg[a]	Log K RLi + C_6H_5I $\uparrow\downarrow$ C_6H_5Li + RI[b]	$E^2{}_{1/2}$ RHgX[a,c]	pK_a RH[d]
c-C_5H_{11}	...	+6.9	...	44
i-C_3H_7	>+6.0	...	3.27	43
i-C_4H_9	+4.3	+4.6	...	41.5
n-C_3H_7	...	+3.9	...	41
C_2H_5	+4.0	+3.5	3.25	40.5
CH_3	+1.8	...	3.10	39
$C_6H_5CH_2CH_2$	+1.0	...	3.04	38
c-C_3H_5	+0.7	+1.0	3.01	38
$CH_2{=}CH$	+0.3	−2.43	2.94	37
C_6H_5	0	0	2.92	37
$CH_2{=}CHCH_2$	−0.4	...	2.32	36.5
$C_6H_5CH(CH_3)$	−0.4	...	...	36.5
C_6Cl_5	...	...	2.36	...
$C_6H_5CH_2$	−0.7	...	2.08	35
$OHCCH_2$	...	...	1.85	...
CH_3COCH_2	...	...	1.86	~20
CH_3O_2C	...	...	1.75	...
$C_6H_5C{\equiv}C$	≪−3.0	...	...	18.5

[a] Present work. [b] Reference 2. [c] *Vs.* Ag|AgClO$_4$ (10^{-3} M) reference. [d] Derived or quoted from the compilations and type calculations of Cram based on the data of McEwen, Streitwieser, Applequist, and Dessy, the M-SAD series.[7]

The equilibrium constant for any pair of R groups may be found by subtracting the log K values shown for the pair. The values shown are not better than ±0.3 log unit. Also shown are similar values taken from Applequist's data.[2] The similarity is remarkable. Given the good correlation elsewhere, the limiting value shown for isopropyl, +6, must be near the correct value, and it certainly is less than +8. The good correlation elsewhere also indicates that the disparity shown by the vinyl group is probably due to experimental error, and the expected closeness of vinyl and phenyl in the metal–metal interchange system suggests that the value for vinyl in this system is the correct one.

As Applequist[2] has pointed out, in the alkyl series the order of carbanion stability is that to be predicted from current concepts of inductive effects, and the position of cycloalkyl, vinyl, and ethynyl systems that to be expected from considerations of electronegativity, or s character content of the specific orbital involved in the charge localization. In agreement again with basic concepts, the effect of the introduction of a β phenyl group into an ethyl radical increases carbanion stability by a factor of 10^3, or viewed alternatively, the introduction of two methylene groups between the C_6H_5 and m, decreases the effect of the phenyl radical by a factor of 10 (a diminution of 1/3 per carbon).

Utilizing the pioneering data of McEwen,[1b] as modified by the work of Streitwieser,[1d,4d] Applequist,[2] and our preliminary data,[3] Cram[7] has calculated a series of assigned pK_a values for alkanes and aralkanes. In the region covered by $K_{\mathrm{Rmg}+\mathrm{C_6H_5hg}}$ and $K_{\mathrm{RLi}+\mathrm{C_6H_5I}}$ it was assumed that a factor of 10 in K represented (at least) one pK_a unit. Calculation of the acidity of cyclohexane *via* this route, from the tie point benzene, leads to a value (pK_a = 44) close to that derived from kinetic data involving H–T exchange, this work spanning the

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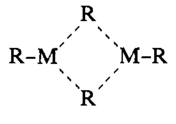
(19) *E.g.*, (α-naphthyl)$_3$B or compounds cited in R. E. Dessy and S. A. Kandil, *J. Org. Chem.*, **30**, 3857 (1965).

(20) R. E. Dessy, T. Psarras, and S. Green, *Ann. N. Y. Acad. Sci.*, **125**, 43 (1965).

(21) R. E. Dessy, F. Kaplan, G. Coe, and R. H. Salinger, *J. Am. Chem. Soc.*, **85**, 1191 (1963).

range of acidities represented by $(C_6H_5)_3CH$ to C_6H_{12} (pK_a = 45). Both calculations were tied back, *via* correlation by competitive metallation equilibria ($RH + A:^- \rightleftharpoons R.^- + HA$), to 9-phenylfluorene (pK_a 18.5) as a base point.[1c] Table I lists the values that can be assigned at present for hydrocarbon acidities using this "M-SAD" system developed by Cram.[7]

Kinetics and Mechanism. Few detailed studies of metal-metal interchange mechanisms have been reported. McCoy and Allred,[22] investigating Me_2M–Me_2M' exchange, reported second-order kinetics, with k relatively independent of solvent dielectric constant. This is indicative of a four-center bridging mechanism



Consistent with this is the report that MeM–Me_2Hg interchanges are extremely slow,[21] Hg preferring a linear bond system which impedes formation of the bridged transition state. The proposal is also consistent with the reports that $(CH_3)_2Mg$–$(CD_3)_2Hg$ interchanges do occur by a process involving transfer of only two alkyl groups at a time, as evidenced by CH_3HgCD_3 intermediacy.[21] Also explicable is the report that donor solvents accelerate Me_2Cd–Me_2Cd^{III} exchange[21] (by labilizing the incipient carbanion) but retard R_3Tl–R_3Tl exchanges (by forming tetracoordinate complexes. However these facts could also be handled by proper consideration of ionic pathways for exchange

$$RMR \rightleftharpoons R:^- + MR^+$$
$$R:^- + R'_2M' \rightleftharpoons RR'_2M^- \rightleftharpoons RM'R' + R':^-$$
$$R':^- + MR^+ \rightleftharpoons R'MR$$

The most powerful support for bridged transition states lies in the numerous reports concerning the retention of stereochemistry at the exchanging site (optical or geometrical) examples being known for Li, Mg, Ga, Tl, Sn, and Hg.[23,24]

Tables II and III report the data supporting the conclusion that the present system, $R_2Mg + (CH_3)_2Hg$, involves reversible second-order kinetics. Testing of the kinetic order between runs by altering initial concentrations yielded excellent agreements of observed k_2.

Table II

$$\underset{(X)}{R_2Mg} + \underset{(Y)}{(CH_3)_2Hg} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2Hg + (CH_3)_2Mg$$
t, glyme

R	t, °C.	X, M	Y, M	k_1 10^4, M^{-1} sec.$^{-1}$	Log $K^{33°}$
C_2H_5	−5	0.55	0.55	31	2.2
	−5	0.72	0.33	37	
i-C_4H_9	33	0.45	0.45	6.1	2.5
	33	0.38	0.75	5.5	

Table III

$$\underset{(\sim 0.5\ M)}{R_2Mg} + \underset{(\sim 0.5\ M)}{(CH_3)_2Hg} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2Hg + (CH_3)_2Mg$$
t, glyme

R	Log $K^{33°}$	t, °C.	k_1 10^4, M^{-1} sec.$^{-1}$	ΔH^*, kcal. mole^{-1}	ΔS^*, e.u.
C_2H_5	2.2	25[a]	400	13	−22
		−5	31		
		−25	4.1		
i-C_4H_9	2.5	25[a]	3.2	13	−29
		33	6.1		
		40	9.0		
		56	31		
neo-C_5H_{11}	Not measurable	33	Too slow to measure	...	...
i-C_3H_7	4.2–5.2	25[a]	120	6	−46
		−11	25		
		−31	8.5		
t-C_4H_9	Not measurable	33	No observable exchange	...	...

[a] Calculated from data obtained at other temperatures.

It is to be noted that a large increase in activation free energy is observed whenever α- or β-methyl substitution is effected. This is a reflection apparently of the decrease in the activation entropy term, although the observation is based on only three accessible kinetic systems. The effect is remarkable, leading to C_2H_5–CH_3 exchange being more rapid than the i-C_3H_7–CH_3 exchange, although K is much larger for the latter. *Any attempt to utilize kinetic methods in establishing carbanion stabilities should therefore be viewed with extreme caution.* The results are in agreement with a four-center transition state for alkyl transfer, since this should permit reflection in the activation free energy of the steric crowding resulting from increasing the bulk of the bridging alkyl moiety. It is not compatible with an ionic mechanism. The reaction rate constant appears to be unaffected by the addition of salts such as $LiClO_4$, or of bases such as pyridine, in stoichiometric amounts. These kinetic results suggest that steric factors do not severely affect K in the Mg–Hg exchange, an occurrence that might result from consideration of the solvated nature of R_2Mg. α and β substitution leads to moderate changes in K (factors of 2 for Et-i-Bu and $C_6H_5CH_2$–$C_6H_5CH(CH_3)$) although k_2 is altered drastically. It is conceivable that steric factors of disproportionate size could affect K as Eastman[20] has suggested for the RLi–C_6H_5I case, and due caution should be taken in extending the series.

Electrochemical Data. Although much effort has been expended on polarography of organomercurials, particularly as an analytical tool, the definitive survey of the details of the electrochemical processes have only recently been given by Hush and Oldham who worked in protic environments using KCl and Et_4NI as supporting electrolyte.[8] Combined with the work of Gowenlock[9] on the chemistry of the isolable intermediate RHg, and the present data, these may be represented as

$$\begin{tikzcd} RHgX \arrow[r, "e"] & X^- + RHg \arrow[r, "e"] \arrow[d] & R:^- + Hg \\ & 0.5Hg + 0.5R_2Hg \arrow[r, "e"] & R:^- + 0.5Hg \end{tikzcd}$$

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(22) C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962).

(23) (a) See A. N. Nesmayanov, "Selected Works in Organic Chemistry," The Macmillan Co., New York, N. Y., 1963; (b) D. Moy, J. P. Oliver, and H. T. Emerson, *J. Am. Chem. Soc.*, **86**, 371 (1964); (c) D. Seyferth and L. G. Vaughan, *ibid.*, **86**, 883 (1964); (d) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958); (e) O. A. Reutov, *Bull. Soc. Chim. France*, 7, 1383 (1963).

(24) *Cf.* G. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

in dimethoxyethane, using Bu_4NClO_4 as supporting electrolyte. The discharge of R_2Hg species is normally in the region of the supporting electrolytes used in previous studies, and even in the present study it is only when R is a group capable of yielding relatively stable carbanions can a polarographic step corresponding to $n = 2$ be observed for R_2Hg.

There is little doubt that the first polarographic step, for uncomplicated cases, involves the ultimate expulsion of halide ion, and the formation of the subvalent species RHg. Hush and Oldham surmised as much from the observation that the $E_{1/2}$ of the first wave ($E^1{}_{1/2}$) was halogen dependent. In the present case this may be established somewhat more rigorously by observing that the first polarographic step, which is electrochemically irreversible and diffusion controlled, with $n = 1$, shows, on triangular voltammetry, using anodic hold, anodic currents at first reversal corresponding to $X^- + Hg \xrightarrow{-e} HgX$ only when the cathodic sweep limit encompasses the first wave of RHgX.

RHg Species. Gowenlock[9] has synthesized a series of solid black metalliclike RHgX species in liquid NH_3 at Pt electrode. The materials are thermodynamically unstable at temperatures above about 0°, yielding Hg and R_2Hg. They give no e.s.r. signal. The structures proposed involve $R\cdot$ imbedded in a Hg lattice, or R^+ in a Hg lattice, with electrons in the conduction band.[24] The possibility of involvement of RHgHgR has not been given due consideration. In any case, in dimethoxyethane, at a mercury pool, controlled potential electrolysis of C_6H_5HgBr, at a potential beyond $E^1{}_{1/2}$ leads to quantitative production of $(C_6H_5)_2Hg$.[25a]

Similar experiments with C_4H_9HgBr, followed by addition of stoichiometric amounts of $HgBr_2$, regenerated quantitatively the C_4H_9HgBr, indicating the formation of $(C_4H_9)_2Hg$ as the first stable product from the discharge of C_4H_9HgBr at the first wave. When optically active *sec*-C_4H_9HgBr[25b] was employed, the *sec*-C_4H_9HgBr resulting from the sequence

$$\underset{[\alpha]^{25}\text{D }11^\circ}{\textit{sec}\text{-}C_4H_9HgBr} \longrightarrow [\textit{sec}\text{-}C_4H_9Hg] \longrightarrow Hg + (\textit{sec}\text{-}C_4H_9)_2Hg \xrightarrow{HgBr_2} \underset{\alpha\,=\,0}{\textit{sec}\text{-}C_4H_9HgBr}$$

was inactive, as indicated. (The last step is known to involve retention of configuration.[25b]) This confirms Gowenlocks[9] results on the solid RHg species at a Pt electrode. As he has pointed out this means that either a route to racemization of R in RHg is available, or the conversion to R_2Hg is accomplished with inversion of the R becoming attached to RHg, schematically $RHg\cdot\cdot R\cdot\cdot Hg$. These possibilities are operationally indistinguishable at the present.

Further insight into the nature of the RHg species at a Hg electrode is gained by observing that when C_6H_5HgBr (Hg^{203}) is electrolyzed the resulting $(C_6H_5)_2Hg$ has less than 10% of the activity in it (Chart I). Control experiments indicate that $C_6H_5HgCl + Hg \rightleftharpoons$ exchange is too slow to contribute to this loss of activity, and exchange of $(C_6H_5)_2Hg$ with Hg is even slower.[26] Therefore sometime prior to conversion to $(C_6H_5)_2Hg$, phenyl group migration occurs according to $(C_6H_5)Hg + Hg' \rightleftharpoons (C_6H_5)Hg' + Hg$. This may be related to the process involved in racemization of the *sec*-C_4H_9 group, suggesting $Hg\cdot\cdot R\cdot\cdot Hg$. It cannot involve free alkyl or phenyl radicals since production of the bisorganomercury species is quantitative in both cases, and no benzene or biphenyl is observed in the aryl case. At the present it seems best to conceive of a skittering radical on the electrode surface, prior to *chemical* decomposition of RHg.

Chart I

$$\underset{288{,}372\text{ c.p.m.}^a}{C_6H_5Hg^{203}Cl} \xleftarrow[\text{POOL}]{Hg} \underset{323{,}719\text{ c.p.m.}}{C_6H_5Hg^{203}Cl} \xrightarrow[\text{glyme}]{e} C_6H_5Hg^{203} \xrightarrow[\text{POOL}]{Hg} \underset{32{,}241\text{ c.p.m.}}{C_6H_5Hg}$$

[a] Samples in standard scintillation equipment were used for counting purposes. The values represent the average of two to four runs, and are summed over seven channels (40 kev. wide) around the photopeak resulting from Hg^{203}. Counting efficiencies were 16.9%. All samples contained the same equivalent amount of organomercurials.

However, the RHg species may suffer *electrochemical* destruction at sufficiently cathodic potentials. Polarography of solutions of C_6H_5HgBr show two well-defined steps, the first of which has been discussed. The second step ($E^2{}_{1/2}$) involves one electron, is irreversible, and does not correspond to the reduction of $(C_6H_5)_2Hg$. Other RHgX species show similar behavior, except that for the majority the bisorganomercury species is discharged beyond the limit set by supporting electrolyte. (The lack of observation of a potential corresponding to $E^3{}_{1/2}$ in RHgX polarograms incidentally sets a limit on the rate of conversion of RHg to R_2Hg.) It may be concluded that the second step therefore corresponds to the reduction of $RHg \xrightarrow{e} R{:}^- + Hg$.

Carbanion Stabilities. The subvalent species RHg is most certainly sparsely solvated, and presumably oriented at the electrode surface with its Hg adsorbed onto the Hg atom interface. Assuming, with reason, relatively small polarization interactions, negligible or nonexistent π-bonding interactions, the obvious lack of steric problems as a result of the large size of Hg, and the extremely low dissociation energy (6 kcal./mole) ascribed to RHg,[27] it seems reasonable to consider the system a good model for reflecting carbanion stabilities *via* electrochemical reduction to the carbanion. Although the step is irreversible, indicating $E^2{}_{1/2}$ has no direct thermodynamic significance, *a priori*, it might be hoped that the compounds were related enough for α to be relatively constant, and for an empirical correlation with carbanion stabilities to be possible.

Table I lists the values of $E^2{}_{1/2}$ obtained, referred to a $Ag|AgClO_4$ (10^{-3} *M*) reference electrode.

Figure 1 shows that for the series an interesting linear region occurs in the plot of $E^2{}_{1/2}$ *vs.* pK_a or $\log K_{ex}$ for the systems described earlier. This is reasonable if one considers for exchange the free-energy change is given

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(25) (a) Although triangular voltammetry of C_6H_5HgBr did not reveal firm evidence for a process $C_6H_5Hg \leftrightarrows C_6H_5Hg^+$, discussions with Professors Mann and Walborsky concerning their work with cyclopropylmercuric halides, where such a process seemed indicated, led to a reexamination of EtHgBr, where $E^1{}_{1/2}$ for the substrate is well removed from halide oxidation–reduction. Triangular voltammetric evidence of an electrochemically reversible process at potentials near $E^1{}_{1/2}$ suggests strongly some form of the subvalent RHg species—RHg, RHgHgR, or $RHgBr^{-\cdot}$. (b) R. E. Dessy, Y. K. Lee, and J. Y. Kim, *J. Am. Chem. Soc.*, **83**, 1163 (1961).

(26) O. Reutov, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 22, 1 (1961).

(27) C. T. Mortimer, H. O. Pritchard, and H. A. Skinner, *Trans. Faraday Soc.*, **48**, 220 (1952).

by $\Delta F = -RT \ln K$, while for an electrode process $\Delta F = -nf\Delta E$. Although the relationship appears to fail badly at the extreme ends, in the pK_a range of 35–40, it may provide a method of quantitatively arriving at a measure of carbanion stability, and over the entire range may provide at least a system for ordering carbanions as to stability. This may be of most value when groups such as CO_2Me or CH_2CHO, are involved, which cannot be explored by already available techniques. This method has permitted the establishment of a rather interesting and consistent pattern of carbanion stabilities in the R_F series. Reduction of R_FHgX at the second wave ($E^2_{1/2}$) gave n values listed: (R_F, $-E^2_{1/2}$, n) CF_3CF_2, 1.58 v., 2; CF_3CFH, 2.02 v., 3; CF_3CH_2, 2.36 v., 3; $(CF_3)_2CF$, 1.14 v. (1 wave only), 2. The sequence in the ethyl series is as expected. The third electron is probably involved with reduction of the fluoroalkenes produced by F^- elimination from the formed or incipient carbanion. In the isopropyl case, the carbanion stability approximates that of chloride ion apparently, only one wave ($n = 2$) being observed.

R_2Hg Compounds. Only those R_2Hg compounds in which extremely stable carbanionic R groupings are involved show diffusion-controlled irreversible polarographic waves $n = 2$. Table IV lists those for which data are available, and it appears that the sequence is that to be expected from our primitive carbanion stability sequence. The approximate constant difference between $E^2_{1/2}$ and $E^3_{1/2}$ suggests that they are measuring the same parameter.

Table IV

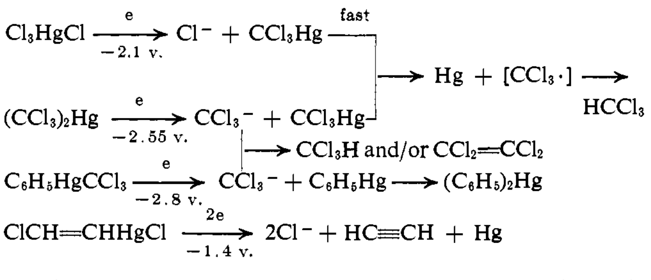
$$R_2Hg \xrightarrow[E^3_{1/2},\ n=2]{\text{glyme}} 2R:^- + Hg$$

R	$E^3_{1/2}$[a]
$CH_2{=}CH$	−3.34
C_6H_5	−3.32
$C_3H_7C{\equiv}C$	−2.90
$C_6H_5CH\overset{t}{=}CH$	−2.75
C_6Cl_5	−2.63
$C_6H_5C{\equiv}C$	−2.25
C_6F_5	−1.81
CCl_3	−1.43

[a] *Vs.* Ag | $AgClO_4$ (10^{-3} *M*) reference.

Unstable RHg Groups. During the course of this survey several examples of very labile RHg species become evident through polarographic and controlled potential electrolysis studies. Chart II shows these results. The decay of CCl_3Hg into $CCl_3\cdot$ and Hg is accompanied by the characteristic development of colloidal black Hg, while the intermediacy of C_6H_5Hg is evidenced by production of $(C_6H_5)_2Hg$. The exact fate of CCl_3^- is difficult to determine since both CCl_3H and $CCl_2{=}CCl_2$ have discharge potentials in the same region. The polarographic detection of chloride ion suggests at least part of the path involves CCl_2 production. That subvalent organomercurials are possibly good carbene precursors is being explored.

Chart II



$$Cl_3HgCl \xrightarrow[-2.1\ v.]{e} Cl^- + CCl_3Hg \xrightarrow{\text{fast}} Hg + [CCl_3\cdot] \longrightarrow HCCl_3$$

$$(CCl_3)_2Hg \xrightarrow[-2.55\ v.]{e} CCl_3^- + CCl_3Hg$$

$$CCl_3^- \longrightarrow CCl_3H \text{ and/or } CCl_2{=}CCl_2$$

$$C_6H_5HgCCl_3 \xrightarrow[-2.8\ v.]{e} CCl_3^- + C_6H_5Hg \longrightarrow (C_6H_5)_2Hg$$

$$ClCH{=}CHHgCl \xrightarrow[-1.4\ v.]{2e} 2Cl^- + HC{\equiv}CH + Hg$$

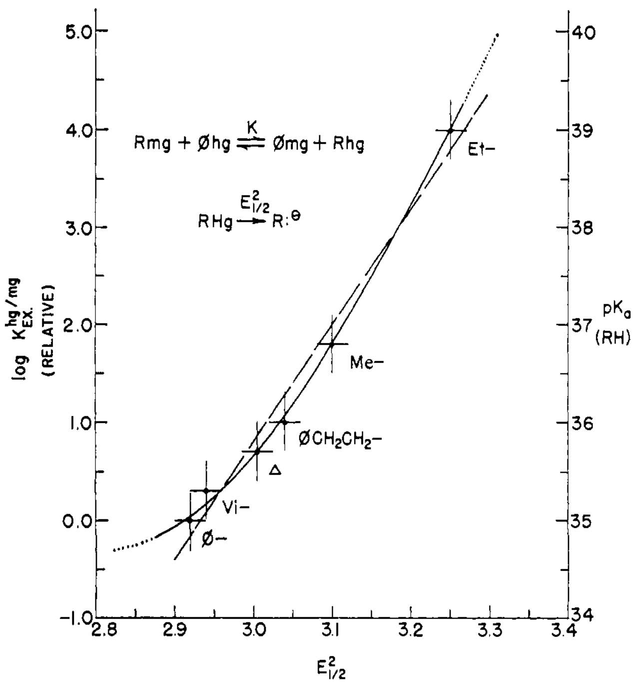
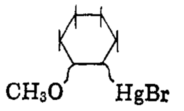


Figure 1.

The decomposition of *trans*-β-chlorovinylmercuric chloride, $ClCH\overset{t}{=}CHHgCl$, into $HC{\equiv}CH$, Hg, and Cl^-, presumably *via* the very transient $ClCH{=}CHHg$, which yields $HC{\equiv}CH$ and HgCl (the latter reducing at the cathodic potential involved), is to be contrasted to the more classically behaved oxymercuration products.



	$E^1_{1/2}$	$E^2_{1/2}$
cis	−1.5	−3.1
trans	−1.7	−2.6

Apparently neighboring group interactions leading to expulsion of CH_3OHg are not favorable, due to the weakness of HgO associations. The relative values of $E^2_{1/2}$ for the two stereoisomers are what might have been predicted for conformationally stable carbanions, the *cis* isomer experiencing some charge–dipole interaction in the transition state leading to the carbanion.

Errata. Although not related to the above, the following study was made possible by the techniques developed during the work already described.

An early report from our laboratory indicated that (A) $C_6H_5HgEt + Hg^*Cl_2 \rightarrow C_6H_5Hg^*Cl + EtHg^*Cl$ (with no exchange found in the necessary control experiments), thus suggesting equivalent Hg atoms in the transition state.[28] Broderson[29] later reported on

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(28) R. E. Dessy, Y. K. Lee, and J. Y. Kim, *J. Am. Chem. Soc.*, **83**, 1163 (1961).

(29) K. Broderson and V. Schlenker, *Chem. Ber.*, **94**, 3304 (1961).

(B) $C_6H_5HgBu + Hg^*X_2 \rightarrow C_6H_5HgX + BuHg^*X$. Nesmeyanov and Reutov[30] finally reported (C) $C_6H_5HgEt + Hg^*X_2 \rightarrow C_6H_5Hg^*X + EtHgX$. The main experimental difficulty is separation of the final products, which has been accomplished by fractional crystallization or precipitation or steam distillation. The fact that C_6H_5HgCl discharges at a more anodic potential

$$C_6H_5HgCl \xrightarrow[e]{-1.15\ v.} C_6H_5Hg \longrightarrow (C_6H_5)_2Hg$$

$$EtHgCl \xrightarrow[e]{-1.55\ v.} EtHg \longrightarrow Et_2Hg$$

than EtHgCl, and that ~10% of a label in C_6H_5HgCl is retained by the $(C_6H_5)_2Hg$ produced suggests that if labeled Hg^*Cl_2 were treated with C_6H_5HgEt, and the solution electrolyzed at −1.15 v., then the resulting solution should contain the following approximate activities for the possibilities described above: A, 60%; B, 100%; C, ≪50%. Table V indicates that there is little doubt that Reutov's results are correct, and that our findings and Brodersons are in error. What activity remains after electrolysis in system 3 is due in large part to only partial electrolysis (85%) of the C_6H_5HgCl. Attempts to recheck the other report of apparent statistical distribution in RHgR′ cleavage (*cis*-2-methoxycyclohexylneophylmercury) failed due to inadequate separation of $E^1_{1/2}$.[31]

Table V

System	C.p.m.[a] Before elect.	C.p.m.[a] After elect.
1, $C_6H_5Hg^*Cl$	244,000	24,000
2, $C_6H_5Hg^*Cl + EtHgCl$	244,000	26,000
3, $C_6H_5HgEt + Hg^*Cl_2$	596,000	120,000

[a] Details are as given in Chart II. The values represent averages of two to four runs.

Experimental Section

Redistributions Reactions. A. Preparation of Compounds. 1. Organomercury Compounds. Diphenylmercury was purchased from Distillation Products, Inc., and recrystallized from benzene. Bisphenylethynylmercury was prepared from phenylacetylene and K_2HgI_4 in ethanol and recrystallized from a benzene-ligroin mixture, m.p. 124°. Diallylmercury was prepared by the method of Revy.[32a] Biscyclopropylmercury and divinylmercury were prepared by the method of Dessy and Reynolds.[32b] All other mercury compounds were prepared from the corresponding Grignard reagents by reaction with $HgCl_2$.

2. Organomagnesium Compounds. Diphenylmagnesium was prepared from diphenylmercury by exchange with magnesium metal in ether.[33] Bisphenylethynylmagnesium was prepared from phenylacetylene and diethylmagnesium. All other dialkyl or diaryl magnesium compounds were prepared from the corresponding Grignard reagent by the dioxane precipitation method.[34] The ether was removed under vacuum and replaced with 1,2-dimethoxyethane (monoglyme). The solutions were standardized by acid titration.

B. Equilibrium Measurements. In a typical experiment, equimolar quantities of the organomercury and organomagnesium compound were introduced under nitrogen atmosphere in an n.m.r. tube and the tube was sealed under vacuum. The n.m.r. spectra were recorded at different time intervals. The spectra were obtained in a Varian Associates A-60 spectrometer. A small capillary tube containing TMS had been inserted previously in the nmr tube as external standard. After equilibrium was attained, the equilibrium constant for the reaction was calculated from the ratio of the integrated areas for the indicated peak pairs R′mg/Rmg or Rhg/Rmg (see Table VI).

Table VI

$$R_2Mg + R_2'Hg \rightleftarrows R_2Hg + R_2'Mg$$

R	R′	*K*, (R′mg)(Rhg)/(R′hg)(Rmg)
$(CH_3)_2CH$	$(CH_3)_2CHCH_2$	*a*
$(CH_3)_2CHCH_2$	CH_3CH_2	2.0
CH_3CH_2	CH_3	100.0
CH_3	*c*-C_3H_5	1.3
CH_3	$CH_2{=}CH$	30.0
CH_3	C_6H_5	60.0
$CH_2{=}CH$	C_6H_5	2.0
C_6H_5	$CH_2{=}CHCH_2$	2.6
C_6H_5	$C_6H_5CH_2$	5.5
C_6H_5	$C_6H_5CHCH_3$	2.5
$C_6H_5CH_2$	$C_6H_5{\equiv}C$	Complete reaction

[a] Almost complete exchange and complicated n.m.r. spectra do not allow accurate calculations.

C. Kinetic Measurements. The rate of the reaction $R_2Mg + Me_2Hg \rightarrow R_2Hg + Me_2Mg$ was measured by following the rate of appearance of Me_2Mg, using TMS as internal standard. A known amount of the R_2Mg compound was introduced in an n.m.r. tube. The equivalent amount of Me_2Hg (mixed with TMS) was introduced in a small capillary tube which had been inserted into the n.m.r. tube. All operations were performed under nitrogen atmosphere. The n.m.r. tube was introduced in the probe of the instrument and left to reach thermal equilibrium. After thermal equilibrium was reached, the inner tube was broken by shaking, the two components were mixed, and the n.m.r. spectrum was recorded. Integrals of the TMS and Me_2Mg peaks were recorded at predetermined intervals (1 or 2 min.). The temperature was measured from the chemical shift of the OH and CH_3 peaks of a standard methanol sample, before and after the run and was found to be constant to within ±1°. The second-order rate constants were calculated by the least-square method. The correlation coefficients within a run ranged from 0.984 to 0.995. The values reported in Table VI are the averages of at least two measurements and are good to within 10%.

Electrochemistry. A. Equipment. The experimental procedures involving polarography and controlled potential electrolysis are as previously described.

B. Preparation of Organomercury Compounds. All organomercury halides were formed from interaction of the appropriate Grignard reagent with HgX_2, or by cleavage of the R_2Hg species with HgX_2, or by cleavage of the R_2Hg species with HgX_2. PhHgEt was prepared as previously described. $HgCl_2$ and C_6H_5HgCl labeled with Hg^{203} were prepared in the reported manner.[25b]

C. Optical Labeling Experiments. *sec*-Butylmercuric bromide was prepared and resolved according to the procedure of Charman, Hughes, and Ingold.[35] A total of 80 mg. of the material in 50 ml. of solution was exhaustively electrolyzed at a potential sufficient to convert it to (RHg). The solution was treated with an equivalent amount of $HgBr_2$ to convert it to the original form. Direct observation on this material in a 1-cm. cell in a Bendix spectropolarimeter, Model 62, showed the presence of no optical activity. Polarographic data indicated quantitative cycling of the organomercury.

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(33) G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 56.

(34) A. C. Cope, *J. Am. Chem. Soc.*, 60, 2215 (1938).

(35) Prepared according to the report of N. B. Charman, E. O. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1121, 1131 (1961).

D. Radiochemical Experiments. 1. Electrolysis of C_6H_5HgCl–phenylmercuric chloride, radiolabeled with Hg^{203}, was exhaustively electrolyzed (25 ml. of a 2×10^{-3} *M* solution) to yield quantitatively diphenylmercury, as evidenced by ultraviolet absorption spectra and polarography. As a control, a similar solution was stirred, without electrolysis for a similar time period. The supernatant liquids in both experiments as well as an original sample of the labeled C_6H_5HgCl solution were counted by standard liquid scintillation techniques by Dr. Byron Branson of Taft Sanitary Engineering Center, U. S. Public Health Service. Counting efficiency (geometry) was 16.9%. Chart I indicates counts/min. summed over the seven channels encompassing the photopeak due to Hg^{203}. The figures represent the averages of two to four experiments.

2. Cleavage of $C_6H_5HgC_2H_5$ with $Hg^{203}Cl_2$ to 0.05 mole of $C_6H_5HgC_2H_5$ in 25 ml. of glyme, which was 0.1 *M* in $(C_4H_9)_4NClO_4$, was initiated under a nitrogen blanket. The solution was permitted to rest for 30 min., sufficient for complete disproportionation to occur. The solution then was electrolyzed under controlled potential conditions such that only the C_6H_5HgCl now present was reduced to the subvalent form. After the passage of 4.9 coulombs, polarographic study indicated that approximately 90% of the C_6H_5HgCl had been discharged, and that the diffusion current of the C_2H_5HgCl was that to be expected from the concentration the *in vitro* synthesis should have yielded. Control experiments involving the electrolysis of $C_6H_5Hg^{203}Cl$ alone, and in admixture with C_2H_5HgCl indicated that the electrolysis of C_6H_5HgCl is not interfered with by the presence of other organomercury species. Chart I indicates the results averaged from two to four runs. Counting procedures are described above.

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Organometallic Electrochemistry. III. Organometallic Anions Derived from Group V Elements

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Abstract: The electrochemical behavior of organic derivatives of group V elements, with particular reference to compounds of the type Ph_2MX, has been studied. The phosphorus compounds give transient radicals which abstract hydrogen from solvent to give Ph_2PH and $PhPH_2$. The arsenic, antimony, and bismuth derivatives lead to Ph_2MMPh_2 presumably *via* radical coupling. Further reduction of the coupled product, Ph_2MMPh_2, gave rise to novel organometallic anions, $Ph_2M:^-$. Some reactions of these anions are reported. The cyclic voltammetric behavior of the diphenylarsenic system is discussed.

Reports on the polarographic reduction of group V organometallics have involved either studies in aqueous solution[1,2] or investigations of phosphonium salts.[3–6] Wagenknecht also explored the electrolytic reduction of triaryl derivatives of group V elements in dimethylformamide.[6] He concluded, after identification of the products of the large-scale electrolytic reduction of triphenylphosphine, that the anion radical formed initially decomposed to phenyl radical and diphenylphosphide anion.

$$Ph_3P + e \longrightarrow Ph_3P^{\cdot-} \longrightarrow Ph\cdot + Ph_2P^- \qquad (1)$$

From determinations of i_d, the diffusion current constant, and the slope of the polarographic wave it was thought that eq. 1 involved a reversible one-electron reduction. In contrast, i_d values indicated a two-electron reduction for the triaryl derivatives of arsenic, antimony, and bismuth.

$$Ph_3M + 2e \longrightarrow Ph_2M^- + Ph^- \qquad (2)$$
$$(M = As, Sb, \text{ or } Bi)$$

The present study was undertaken to investigate the possible preparation and properties of subvalent organometallics (by electrolytic reduction) derived from systems of the type

$$R_2MX + e \longrightarrow R_2M\cdot + X^- \qquad (3)$$

(R = organic radical; X = halide or acetate; M = P, As, Sb, or Bi)

Electrolytic reductions were achieved at a stirred mercury cathode in anhydrous glyme, using tetrabutylammonium perchlorate as supporting electrolyte. Controlled potential coulometry, polarography, ultraviolet spectroscopy, and cyclic voltammetry were employed to elucidate the fate and nature of the subvalent species $R_2M\cdot$. Five possible pathways were available to the $R_2M\cdot$ species in this system: (a) stability, (b) coupling to give R_2MMR_2, (c) abstraction of hydrogen from solvent to give R_2MH, (d) arylation of the mercury pool, and (e) disproportionation.

Examples of coupling and abstraction were observed. When coupling occurred, a further reduction of R_2MMR_2 to novel organometallic anions took place.

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