pounds when used as initiators of vinyl polymerization.[6] The high reactivity of benzyllithium in halogen-substitution reactions[7] is also in agreement with a high nucleophilicity for this species.

The rates of reaction 1 do not follow the expected order of relative organolithium basicities,[8] although correlations between rate constants and equilibrium constants within a series of like reactions are known.[9] A well-studied example is that rates of metalation by a given base are proportional to the acidity of the hydrogen which is replaced.[10] In contrast, rates of metalation of RH by different organolithium bases presumably are not controlled solely by the base strength of the metalating reagent. Other nucleophilic displacement reactions on hydrogen also fail to obey the general rate-equilibrium parallelism.[11]

A factor also anticipated to be important in regulating the relative reactivity of organolithium compounds is their degree of clustering in solution.[12] The existence of n-butyllithium as hexamers in benzene solution[13] results in a kinetic dependence for metalation[14] or initiation of polymerization[15] of $[n\text{-butyllithium}]^{1/6}$ in this solvent. Measurements of the order of reaction 1 with respect to organolithium reagent, within the concentration range 10^{-2} to 10^{-1} M total RLi reagent, indicate that benzyllithium, allyllithium, and phenyllithium are reacting as monomeric species, whereas clustering appears to be dominant with n-butyllithium, methyllithium, and vinyllithium.[16] Styryllithium, which should behave similarly to benzyllithium, is reported to react as a monomeric species in the presence of THF.[17] That the reactivity of an organolithium compound may vary with concentration, which in turn may depend on its propensity to self-associate, is indicated by the observation that 0.1–0.5 M benzyllithium is stable in THF solution, whereas at 10^{-2} M it decomposes, presumably by reaction with THF.

Since there are only small differences in organolithium concentrations used in the kinetic experiments reported here and those used by Gilman and McNinch,[1] it is unlikely that varying degrees of aggregation are responsible for the differences in the orders of relative reactivities of the RLi reagents. A possible explanation for the differing reactivity scales is that the product yields of Gilman and McNinch[1] reflect the equilibrium situation and are not a measure of the rate of metalation.

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More detailed kinetic studies will be reported soon.

THE DOW CHEMICAL COMPANY   RICHARD WAACK
EASTERN RESEARCH LABORATORY   PETER WEST
FRAMINGHAM, MASSACHUSETTS

Zero-Charge Potentials of Solid Metals

Sir:

A new method has been devised for measuring zero-charge potentials (z.c.p.) of solid metals. The principle of this method is the same as that of the streaming mercury electrode; a transitory fresh metal surface is produced over the entire electrode, and the open circuit potential is measured before subsequent reactions can appreciably change the electrode charge.[1] The method of getting zero charge on the electrode is possible because the high activation energy for transfer of charge across the inner Helmholtz double layer enables one to measure the pre-existing potential. The simple inorganic ions are under equilibrium conditions during the entire process.

The method of producing fresh metal surface is that of scraping away the entire old metal surface. The apparatus consists essentially of a very high speed rotary scraper.

For the open circuit electrode we write

$$\frac{dq_m}{dt} + i_{cath} - i_{anod} = 0 \tag{1}$$

where q_m is the charge on the electrode, and i_{cath} and i_{anod} are the cathodic and anodic Faradaic processes occurring at the electrode–solution interface. The condition at the transient peak for the electrode potential, E, to be equal to z.c.p. is that

$$|(i_{cath} - i_{anod})\Delta t| < \Delta q_m \tag{2}$$

where Δq_m is the accuracy to which q_m is being measured and Δt is the shortest measurable time increment over which E should not change appreciably. This means that the new surface must be completely produced and potential recordings made in times less than Δt. Thus, the limitation of the method depends on the relative values of the velocity of the experimental procedures and of $(i_{cath} - i_{anod})$.

Zero-charge potentials have been obtained for several noble metals in 0.1 N KCl (*cf.* Table I). These values are in general agreement with values reported in the literature.

TABLE I

Metal	Z.c.p. (*vs.* n.h.e.)
Pt	-0.40 ± 0.05 (pH 12)
Ag	-0.80 ± 0.05 (pH 7)
Cu	-0.35 ± 0.05 (pH 7)
Au	-0.09 ± 0.05 (pH 7)

(1) This method should be distinguished from the Billiter method.

RATE PROCESS INSTITUTE   T. N. ANDERSEN
UNIVERSITY OF UTAH   R. S. PERKINS
SALT LAKE CITY 12, UTAH   H. EYRING