

Table I. Analyses of Gas-Phase Composition Over 0° Films

Substrate	P, torr	Blank (HD), %	Exposed time, hr	% H ₂	% D ₂	% HD
Al ₁	150.3	0.3	10.2	68.9	30.2	0.9
Al ₂	357.7	0.5	11.5	50.0	48.5	1.5
Al ₃	390.9	0.5	14.8	36.7	61.4	1.9
Glass	357.6	0.7	9.98	59.1	39.1	1.8
Ni ₁	348.8	0.7	8.51	28.1	46.6	25.3
Ni ₂	367.0	0.7	9.34	32.0	17.9	50.1
Al + H ₂ O	150.7	0.7	10.2	49.4	47.8	2.8

and procedures for making clean aluminum films were developed. Aluminum of 99.999% purity was evaporated from rigorously pretreated, 20-mil tungsten helices. A very dense, smooth film of aluminum was evaporated onto 273°K substrate by heating the tungsten helix with 12 amp (ac) for 30 sec. During evaporation the pressure rose to values of $\sim 10^{-8}$ torr, but fell back to 10^{-9} torr within 30–60 sec. Electron microscopy of these films revealed them to be made up of relatively uniform crystallites of roughly hexagonal shape, about 0.5 μ in cross section with a few larger crystallites scattered throughout. These clean aluminum films were exposed to hydrogen and deuterium premixed behind a Granville–Phillips bakeable high-vacuum valve. The gases used in these experiments were obtained in 1-l. Pyrex flasks from the Air Reduction Co. The hydrogen was of 99.999% purity and the deuterium contained up to 2% H₂. For each experiment, a new mixing manifold was fused to the gas-handling system. Variation in the H₂/D₂ ratio is due to unequal flask and manifold volumes.

At the end of evaporation the pumps were isolated *via* another bakeable valve where the mixed gases were permitted to impinge on a freshly deposited film and the entire chamber permitted to communicate through a break-seal with a Wallace and Tiernan precision dial manometer.

A series of experiments in which the mixed H₂–D₂ pressures varied from 150.3 to 390.9 torr were conducted. In each case the substrate was maintained at 273°K. An identical filmless run was made, and similar runs were made with clean nickel films. At different intervals, gas-phase samples were taken and analyzed *via* low-temperature gas chromatography over 4-A molecular sieves. Another run was made in which the clean aluminum was first allowed to react with a small quantity of water vapor prior to treating with the premixed gases.

No evidence for chemisorption of hydrogen on clean aluminum at 273°K was forthcoming from these experiments. Within experimental limits, the baked glass substrate brought about as much H₂–D₂ conversion as did the aluminum films. Nickel films in the same experimental regime resulted in order of magnitude increases in conversion. The results of typical runs are shown in Table I.

An aluminum film exposed, prior to dosing with H₂ and D₂, to 2–3 mm of water vapor for several minutes gave increased conversion. The film was exposed to water vapor, which was then pumped out to forepump pressures ($\sim 10^{-4}$ torr). The system was closed off and only long-term exposure to mixed gases measured. For a blank of 0.7% HD, the exposure of this film to equimolar H₂ and D₂ for 10.2 hr at 150 torr resulted in conversion of 2.8%.

Clean aluminum exposed to large quantities of hydrogen at 273°K shows no evidence of chemisorption; however, if hydrogen chemisorption were an activated process, its absence at this temperature does not preclude chemisorption at higher temperatures. Data on chemisorption deduced from ortho–para^{7–8} changes are suspect because dissociative adsorption is not uniquely required for this process. Isotopic exchange, on the other hand, is a specific indication that dissociative chemisorption has taken place.

Our findings support those of Trapnell⁵ and others⁶ to the conclusion that aluminum does not chemisorb hydrogen, and it is believed that further systematic pursuit of this research will definitely assign the ortho–para conversion catalysis to contaminant films of aluminum oxide.

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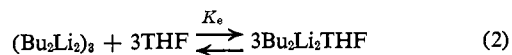
Solvent Effects in Organometallic Reactions. VI. A Kinetic Role of Base

Sir:

Application of eq 1 to analyze initial reaction rates, R_i , of organolithium reagents, RLi, with a number of different substrates, Z, in several basic solvents reveals that there is a common *kinetic role* for solvent, the second role of base in these reactions. The first,

$$R_i = k[\text{base}]^{\alpha}[\text{RLi}]^{\beta}[\text{Z}]^{\gamma} \quad (1)$$

a *thermodynamic role*,¹ is illustrated in eq 2; a base such as tetrahydrofuran, THF, reacts with an oligomer such as butyllithium hexamer, (Bu₂Li)₃,² to form a specific lithium dimer coordination complex, Bu₂Li₂·THF. The fugacity of the base is slight in this complex; THF has negligible vapor pressure over



benzene solutions of BuLi if the base/lithium ratio, r , is less than 1/2.³ Because this thermodynamic role thus consumes some solvent, when r exceeds 1/2, the effective base, [base]_e, for the kinetic role is the difference between total base and half the total lithium; e.g., [THF]_e = [THF] – 1/2[BuLi]. Sub-

(1) G. W. Gibson and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

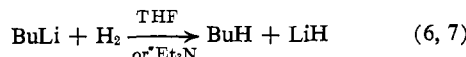
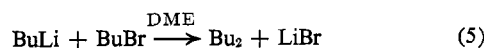
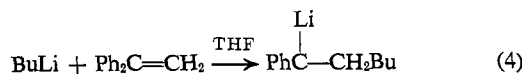
(2) D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

(3) For excellent kinetic data revealing the significance of an r value of 1/2 see Ye. A. Kovriezhnikh, V. M. Basmanova, and A. I. Shatenstein, *Org. Reactivity, Tartu State Univ.*, **1**, 103 (1964); A. I. Shatenstein, Ye. A. Kovriezhnikh, and V. M. Basmanova, *ibid.*, **2**, 135 (1965)

stitution in the log form of (1) shows that at constant initial lithium and substrate concentrations, $\log R_i$ and $\log [\text{base}]_e$ could vary linearly (eq 3) with the slope α , which is a kinetic order in base.

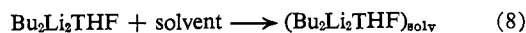
$$\log R_i = \alpha \log ([\text{THF}] - \frac{1}{2}[\text{BuLi}]) + C \quad (3)$$

Experimental data on the effect of THF on the addition rate of BuLi to diphenylethylene (eq 4) in benzene was obtained by Waack, Doran, and Stevenson but was not quantitatively analyzed.⁴ Line 4 of Figure 1 shows our treatment (eq 3) of their data obtained with $[\text{BuLi}] \text{ ca. } 0.02 \text{ M}$ and varying $[\text{THF}]$, 0.02 to 0.36 M. Other lines in Figure 1 show analogous treatments of Shatenstein's data on coupling between BuLi and BuBr in hexane with dimethoxyethane (eq 5)³ and of our own data on BuLi hydrogenolysis in benzene with THF (eq 6) and with triethylamine (eq 7). The kinetic order in each case, slope α , is approximately unity. In other words, *three entirely different reactions, addition, coupling, and lysis, have rates which are directly proportional to quantities of base available.*



Generally accepted mechanisms for the common reactions of organometallic reagents (*e.g.*, addition, coupling, and lysis) involve covalency changes by movement of paired electrons (Lewis acid-base mechanisms). Rate accelerations of such reactions by the better electron donors (Lewis bases), relative to weaker bases or to hydrocarbons, have been interpreted in terms of a better metal cation (Lewis acid) solvation which facilitates reaction of a carbanion (Lewis base) from the reagent. Reactions of lithium reagents have been interpreted this way repeatedly.⁵

This interpretation of ionization to carbanions is neither consistent with solvent effects on physical properties of lithium alkyls themselves nor adequate to explain the kinetic role of base on reaction rates of these reagents. The thermodynamic role of base, formation (eq 2) of the specific lithium dimer coordination complex, does cause a slight increase in reagent polarity. However, additional basic solvent does not enhance that polarity, does not dissociate the lithium dimer, but rather solvates (eq 8) the complex so as to actually mask its apparent (macroscopic) polarity.



The many physical properties of lithium alkyls we have studied in solutions of increasing r (base/Li ratio) are generally characteristic of the ground state, and none changes significantly after r is about 1/2, with one exception. The exception is electronic spectra, the one property particularly characteristic of excited

(4) R. Waack, M. A. Doran, and P. E. Stevenson, *J. Organometal. Chem.* (Amsterdam), **3**, 481 (1965).

(5) Cf. C. E. H. Bawn and A. Ledwith, *Quart. Rev.* (London), **16**, 382 (1962); G. Wittig, *Experientia*, **14**, 389 (1958); R. Waack and P. West, *J. Am. Chem. Soc.*, **86**, 4495 (1964); J. F. Eastham and G. W. Gibson, *J. Org. Chem.*, **28**, 280 (1963); R. E. Dessy and F. Paulik, *Bull. Soc. Chim. France*, **7**, 1378 (1963).

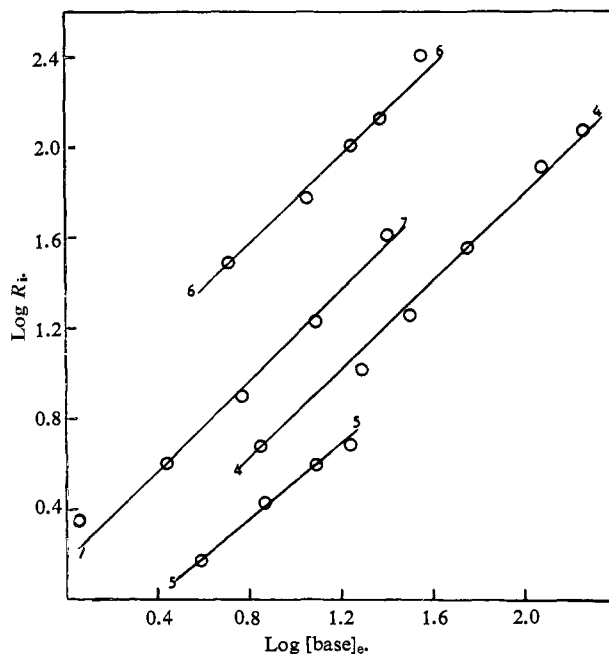
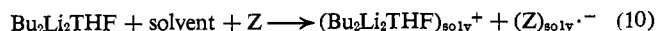


Figure 1. Initial rate data plotted along numbered lines are from BuLi reactions shown in corresponding eq 4-7. Effective base concentrations, $[\text{base}]_e$, where calculated as the difference between $\frac{1}{2}[\text{BuLi}]$ and the total base; *e.g.*, *cf.* eq 3. The slope, α , of each line is 1.0 ± 0.1 .

states. Excess basic solvent and BuLi gives rise to broad absorption which extends from the ultraviolet into the visible and is characteristic of charge transfer. This charge transfer to solvent is primitively represented by



We propose (as an alternative to dissociation or ionization to carbanions) that the primary reaction process of lithium alkyls is one of charge transfer (CT) from the associated reagent and (as an alternative to exclusive Lewis acid-base steps in their reactions) single electron-transfer steps (SET mechanisms). It follows that, in considering solvent support for *organometallic reactions*, one must specifically consider anion (not just cation) solvation, *e.g.*, formation of the solvated electron. Reaction of a lithium reagent by CT to substrate is represented by⁶



It is our hypothesis that the kinetic role of base is charge-transfer support. Each solvent system (basic solvent itself or concentration of that base in a hydrocarbon) may have a characteristic leveling effect on SET reaction rates, those rates being limited by the ability of the solvent system to support CT. One may view this support as a requirement of a finite quantity of base to transfer each electron and/or to solvate each SET transition state or intermediate. In other words, the number of electrons transferred per unit time may

(6) The subject of electron transfer from lithium reagents has been recently reviewed: C. G. Screttas, Doctoral Thesis, University of Tennessee, 1966. The first recognized formation of a radical anion by reaction of a metal alkyl was Schlenk's conversion of benzophenone to a ketyl, which was identified by its color and dimerization: W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916). In 1962 the first esr spectral identification of radical anions generated by BuLi was reported: H. W. Brown and R. C. Jones, *J. Chem. Phys.*, **37**, 1571 (1962); since then lithium alkyls have been used in this and several other laboratories to generate esr spectra.

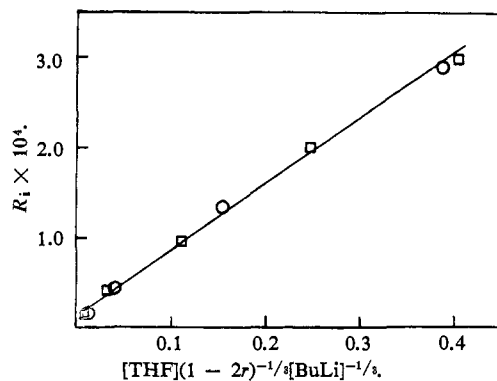


Figure 2. Initial rates of reaction 4 as the function of $[\text{THF}]_e$ given in eq 11 with $[\text{BuLi}]$ 0.15 M (O) and 0.30 M (\square).

not be a function of the concentration of the source for those electrons (at least above a certain lower limit of source concentration), but rather may be a function of the number of available basic molecules. One could even say that, for a given system, each CT process requires a certain volume of the system.

If our hypothesis is valid, an obvious consequence is that *some reactions of lithium reagents will be kinetically independent of reagent concentrations*. Precisely this result is found in BuLi addition (eq 4) rates in excess THF, *i.e.*, when $r > 1/2$; the published⁴ data show that R_i does not increase with increasing $[\text{BuLi}]$. With $[\text{THF}]$ constant and $r > 1/2$, additional R_i values are essentially constant with increasing $[\text{BuLi}]$, until this reagent concentration approaches $1/2[\text{THF}]$, and then R_i decreases; *i.e.*, when a significant portion of the base is consumed in complexation, R_i decreases. Another critical test of the hypothesis can be made with R_i values from runs without excess THF, *i.e.*, $r < 1/2$.

Equation 11, derived by a conventional algebraic treatment of equilibrium 2, gives $[\text{THF}]_e$ when $r < 1/2$. Although the effective base concentration is then extremely small, because K_e for (2) is large, the addition (4) rate is still clearly proportional to $[\text{THF}]_e$ as shown in Figure 2. The addition rates plotted show their linear dependence on $[\text{THF}]_e$ and their independence of $[\text{BuLi}]$; the data cover runs at two $[\text{BuLi}]$ values, 0.15 and 0.30 M, with a 30-fold variation in total THF concentration, 0.0025 to 0.074 M.

$$[\text{THF}]_e = \frac{[\text{THF}]}{(6)^{1/3}(K_e)^{1/3}(1 - 2r)^{1/2}[\text{BuLi}]^{1/3}} \quad (11)$$

Elucidation of every detailed step in SET reactions may prove difficult, but we feel the general concept of solvent support of CT has obvious utility in rationalizing many diverse phenomena now.

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The Novel Structure



Sir:

The chelating properties of ditertiary arsines and phosphines have been extensively studied, most notably by Chatt, Nyholm, and their co-workers.^{1,2} Two new

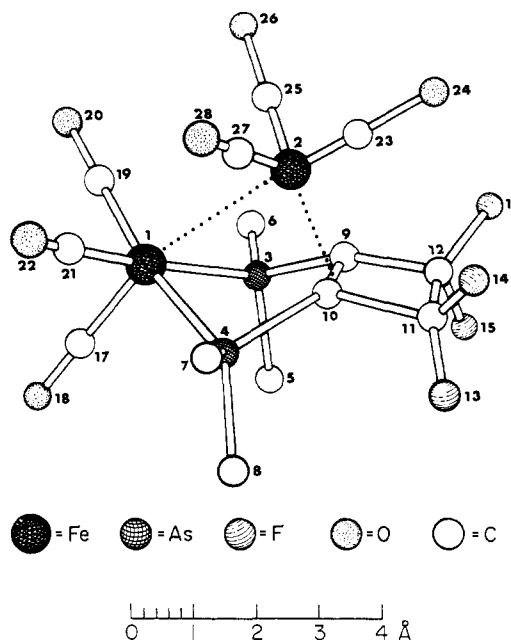


Figure 1.

ligands of this type, $\text{RC}=\text{C}(\text{R})\text{CF}_2\text{CF}_2$ ($\text{R} = \text{AsMe}_2$, PPh_2) are being investigated. These cyclobutenes are similar to the *o*-phenylene compounds, in that they displace carbon monoxide from simple metal carbonyls to give compounds of the type $\text{LMo}(\text{CO})_4$, $\text{LFe}(\text{CO})_3$, $\text{LNi}(\text{CO})_2$; reaction also occurs with noble metal halides yielding complexes of the expected type. Details of these compounds will be given elsewhere, the purpose of the present note being to report the isolation, during the preparation of $\text{LFe}(\text{CO})_3$ ($\text{L} =$ the diarsine), of an unusual compound for which X-ray crystal analysis has given the molecular formula $\text{L}\{\text{Fe}(\text{CO})_3\}_2$ and the structure shown in Figure 1.

Crystals of the compound are monoclinic: $a = 9.37$, $b = 14.15$, $c = 14.82$ Å; $\beta = 96.1^\circ$; space group Cc or $C2/c$. The density, 2.02 g cm^{-3} by flotation, is consistent with a unit cell content of four molecules of molecular weight 614 (later mass spectrometric measurement gave 612). The structure was determined from the three-dimensional Patterson function, which indicated space group Cc , and from electron-density maps, using $\text{Mo K}\alpha$ scintillation counter data for 900 reflections. Least-squares refinement has given $R = 0.057$.

The geometry of the molecule is illustrated in Figure 1, which, together with the bond distances and angles given in Table I, indicates that the structure may best be described in terms of two linked iron atoms. One iron atom is octahedrally coordinated to three carbonyl groups and the two arsenic atoms, with the sixth position occupied by the Fe-Fe bond. The second iron atom has trigonal bipyramidal coordination, the equatorial positions involving two carbonyl groups and the π bond from the cyclobutene system, with the apical positions occupied by the third carbonyl group and the Fe-Fe bond. The molecule has approximately C_s symmetry.

The Fe-Fe distance, 2.88 Å, is longer than those of about 2.69 Å in other compounds with nonbridged

(1) G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).

(2) T. A. Manuel, *Advan. Organometal. Chem.*, 3, 181 (1965).