

effective at pH values as low as 2.7. As reaction 14 gains in importance, terminating reaction 13 diminishes in importance. Consequently, $G(\text{CO}_2)$ rises with increasing pH.

Therefore, on the basis of our kinetic evidence, the pK of ionization reaction 12 may be 2.5 ± 0.5 . This conclusion is supported by recent pulsed electron beam studies of the aqueous formic acid and carbon dioxide systems.¹¹ In each of these systems one transient absorbing species with $\lambda_{\text{max}} \sim 2600 \text{ \AA}$. forms in solutions in the pH range from 3.5 to 6.25. Below pH 2.5, not only is the intensity of this band greatly diminished, but the second-order decay is also altered, facts that support our conclusion about the ionization of the carboxyl ion.

The decrease in $G(\text{CO}_2)$ above pH 4.4, after nearly complete ionization of formic acid and the carboxyl radical, indicates further modification in the mechanism. Since the pK^{12} of the HO_2 radical is 4.5 and corresponds almost exactly with our maximum $G(\text{CO}_2)$, we suggest participation of O_2^- as an important terminating species. A possible reaction is $\text{CO}_2^- + \text{O}_2^- \rightarrow \text{CO}_2 + \text{O}_2^{2-}$,

(11) E. J. Hart and S. Gordon, unpublished results.

(12) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).

which may be relatively much faster than $\text{CO}_2^- + \text{HO}_2 \rightarrow \text{CO}_2 + \text{HO}_2^-$, thereby shortening the kinetic chain length of reaction sequence 6 and 14. Until further information is available on the rate constants of these termination processes, further speculation seems unwarranted.

The decrease in $G(\text{CO}_2)$ above pH 10 is probably associated with the ionization of the hydroxyl radical previously postulated to explain the chain conversion of $\text{O}^{16}\text{O}^{18}$ to $\text{O}^{16}\text{O}^{16}$ in alkaline solutions.¹³ Recent work has shown that the pK for OH dissociation is 11.9.¹⁴ Under these conditions, if the ratio $k_{\text{O}^- + \text{H}_2\text{O}_2} / k_{\text{O}^- + \text{HCOO}^-}$ is greater than the ratio $k_{\text{OH} + \text{H}_2\text{O}_2} / k_{\text{OH} + \text{HCOO}^-}$, $G(\text{CO}_2)$ will decrease with increasing pH. Ionization of hydrogen peroxide may be involved at pH values above 11, too.

Acknowledgment. A. H. gratefully acknowledges a fellowship and maintenance from the Agency for International Development, Washington, D. C., and from the Pakistan Atomic Energy Commission, Karachi.

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Kinetics of Addition of Vinyl lithium to 1,1-Diphenylethylene in Tetrahydrofuran Solution

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From a kinetic analysis of the reaction, $\text{CH}_2=\text{CHLi} + \text{CH}_2=\text{C}(\text{C}_6\text{H}_5)_2$ (THF) \rightarrow $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)_2\text{Li}$, it is concluded that vinyl lithium is aggregated in tetrahydrofuran solution. Over a vinyl lithium concentration of 5×10^{-3} to $2 \times 10^{-1} M$ the kinetic law $dA/dt = k'[\text{DPE}][\{\text{ViLi}\}_i/3]^{1/3}$ is obeyed, where $k' = 5.7 l.0.34 \text{ mole}^{-0.34} \text{ hr.}^{-1}$ and $\{\text{ViLi}\}_i$ is the total initial concentration. Rates were measured spectroscopically.

The relative reactivities of organolithium compounds as polymerization initiators¹ or as metalating reagents² in tetrahydrofuran solution are found to vary markedly with their structure. Changes in reactivity with structure are probably, in part, a consequence of inherent reactivity differences. Effective reactivities might also vary owing to different extents of aggregation of the organolithium reagents,^{2,3} presuming that the associated form is unreactive relative to the less associated reagent.

Vinyl lithium is one of the least reactive of the simple organolithium reagents.^{1,2} For example, it is less reactive than *n*-butyllithium, benzyl lithium, allyl lithium,

and phenyllithium. The rate of addition of vinyl lithium to 1,1-diphenylethylene (DPE) in tetrahydrofuran (THF) solution is slow enough to be followed by spectroscopic techniques. In contrast, *n*-butyllithium adds to DPE essentially instantaneously under these conditions.

The majority of kinetic measurements reported for organolithium compounds have concerned *n*-butyllithium in hydrocarbon solution.⁴ These kinetic experiments, which are substantiated by colligative measurements,⁵ establish that *n*-butyllithium is predominantly hexameric in hydrocarbon solution throughout the concentration range 10^{-4} to $3 M$. Ethyllithium is also indicated to be hexameric in hydrocarbon solution,⁶ and *t*-butyllithium is reported to be tetrameric.⁷

There are no reported physical measurements of the degree of aggregation of organolithium reagents in

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(6) J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

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THF solution. The only previous kinetic studies reported for organolithium compounds in solutions containing THF are the *n*-butyllithium-initiated polymerizations of styrene⁸ and isoprene.⁹ First-order dependence of propagation on RLi show that polystyryllithium and polyisoprenyllithium are predominantly monomeric in the presence of THF. In less polar solvents, *i.e.*, hydrocarbons, these species are reported to be dimeric.

In contrast, the kinetic experiments reported here establish that vinylolithium is predominantly associated in THF. Thus, the propensity of an organolithium compound to aggregate is dependent on its structure as well as the solvent. Organolithium reagents having lower effective reactivities are indicated to be more extensively aggregated. Differences in extent of association are, therefore, expected to influence effective reactivities of organolithium compounds in THF solution.

Experimental

The spectroscopic cell used for these oxygen- and moisture-sensitive systems was described previously.¹⁰ Vinylolithium was prepared in *n*-hexane solution from tetravinyltin *via* transmetalation with *n*-butyllithium.¹¹ The insoluble vinylolithium was washed twice with dry hexane (distilled from lithium aluminum hydride) before dissolving it in THF. The *n*-butyllithium used in the preparation of vinylolithium was obtained from Foote Mineral Corp. in hexane solution.

THF was freshly distilled in argon from lithium benzophenone ketyl. 1,1-Diphenylethylene (DPE) was vacuum distilled from calcium hydride and shown to be pure by g.l.c.

Spectra were taken on a Cary Model 14 recording spectrophotometer equipped with an automatic programming unit.

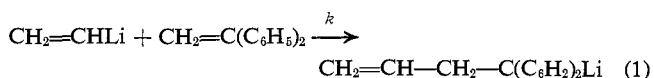
In a typical experimental run the absorption-cell apparatus was oven dried, evacuated to high vacuum, flushed with argon, re-evacuated, and filled with a positive argon pressure. Reagents were added *via* Hamilton gas-tight syringes.¹⁰ A THF base line was read, DPE was added, and in some experiments any contaminating substances were quenched by dropwise addition of *n*-butyllithium until a permanent faint color appeared. This usually consumed 1–5% of the DPE. A spectrum was taken to establish a base line and determine the concentration of DPE from its strong absorption at 250 m μ ($\log \epsilon = 4.04$). The desired amount of vinylolithium was added, and the optical density at wave length 486 m μ was scanned continuously. After 1 hr. the spectrophotometer was programmed to scan from 550 to 400 m μ at 30-min. intervals. In this manner absorbance (*A*) *vs.* time curves, as shown in Figure 1, were obtained. Initial reaction rates were determined from the slope of these reaction curves. The temperature was 21 \pm 1°.

Results

The rate of addition of vinylolithium to DPE in THF

solution is found to be first order in DPE and one-third order in vinylolithium.

Vinylolithium adds to 1,1-diphenylethylene to form 1,1-diphenyl-3-butenyllithium,¹⁰ having λ_{\max} 486 m μ in THF solution.



Initial reaction rates are given in Table I. In most of these experiments vinylolithium was in excess.

Table I. Kinetic Data for Reaction 1

Expt.	(DPE) _i , M × 10 ³	{ViLi} _i , M	(dA/dt) _i , O.D.U./hr. ^a	(dA/dt) _i ^b , (DPE) _i , hr. ⁻¹	k', ^c l. ^{0.34} , mole ^{-0.34} , hr. ⁻¹
122	9.3	0.105	2.2	1.71	5.24
126	7.9	0.092	2.0	1.83	5.84
127	8.7	0.102	2.2	1.83	5.65
128	8.3	0.014	0.91	0.80	4.76
133	8.3	0.050	1.73	1.51	5.90
134A	3.7	0.0063	0.43	0.84	6.55
134B	12.4	0.0050	1.06	0.62	5.20
137	7.9	0.0132	1.07	0.98	5.96
158a	7.6	0.23	2.6	2.5	5.89
158b	7.9	0.057	1.93	1.93	6.63
158c	7.9	0.0091	0.85	0.78	5.38
					Av. k' = 5.73
					Std. dev. = 0.56

^a Path length = 0.0046 cm.; O.D.U. = optical density units.

^b Rate of adduct formation in concentration units of moles/l. ^c k' = (dA/dt)/[(DPE)_i{ViLi_i/3}]^{1/3}.

The kinetic and rate expressions are analogous to those obtained for *n*-butyllithium in hydrocarbon solution.⁴ Relatively unreactive vinylolithium aggregates are in equilibrium with a more reactive, less associated form (probably *n*-mer \rightarrow monomer).

For $n^{-1}(\text{ViLi})_n \rightleftharpoons \text{ViLi}$, $K = [\text{ViLi}]/[(\text{ViLi})_n]^{n^{-1}}$. The rate of reaction 1 will be $dA/dt = k[\text{DPE}][\text{ViLi}]$, which, on substituting for monomeric ViLi with $k' = kK$ and $(\text{ViLi})_n = \{\text{ViLi}\}_i/n$, where $\{\text{ViLi}\}_i$ is the total initial concentration, results in $(dA/dt)_i = k'[\text{DPE}][\{\text{ViLi}\}_i/n]^{n^{-1}}$.

A plot of $\log(\text{rate}_i/\text{DPE}_i)$ *vs.* $\log \{\text{ViLi}\}_i$ will be of slope n^{-1} and have an intercept of $\log k' + n^{-1} \log n^{-1}$. This is shown in Figure 2.

The regression line¹² of Figure 2 is $Y = 0.34X + 0.608$, indicating the most probable value of *n* is 3. For comparison, lines for *n* = 2 and 4 are drawn in Figure 2 passing through the mean of the data. The standard deviation from regression ($S_{y,x}$) is ± 0.086 , and the standard deviation of the slope (S_b) is ± 0.047 . The probability of these experiments belonging to a set in which $n \neq 3$ but *n* = 2, 4, 5, or 6 is 0.8, 8.1, 1.7, and 0.5%, respectively. As *n* becomes larger, the change in slope is smaller, and larger *n* values are more difficult to distinguish. This analysis establishes that vinylolithium at concentration 5×10^{-3} – 10^{-1} M is associated in THF solution and indicates that the more reactive kinetic species is one-third that of the vinylolithium aggregates which predominate in solution.

From the intercept of Figure 2, *k'* is calculated to be

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 (11) D. Seyferth and M. A. Weiner, *ibid.*, **83**, 3583 (1961).

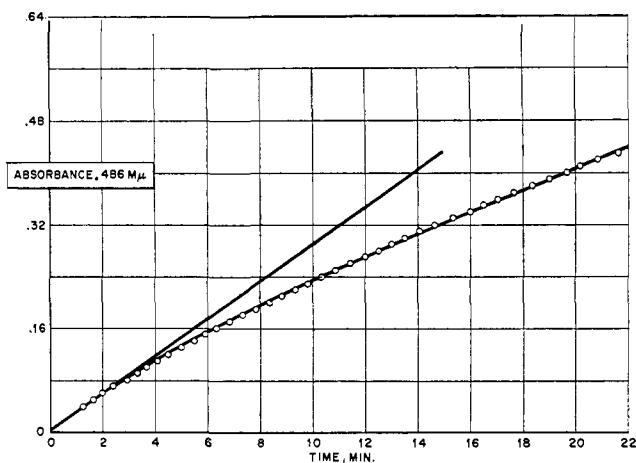


Figure 1. Initial rate curve for reaction 1, $\text{ViLi} + \text{DPE} \rightarrow \text{adduct}$. $\lambda_{\text{max}} 486 \text{ m}\mu$.

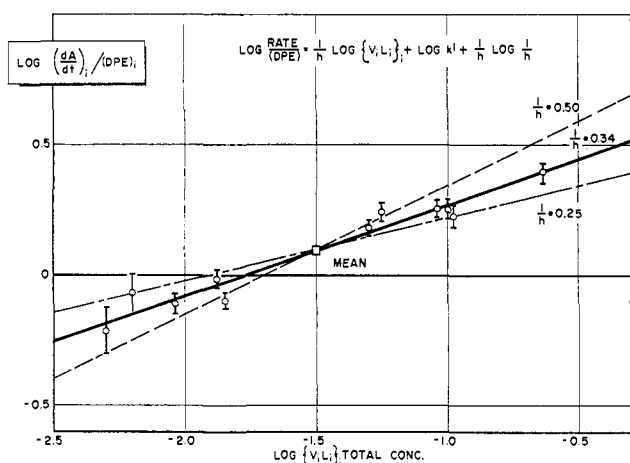


Figure 2. Order of reaction 1 in vinyl lithium.

$5.86 \text{ l.}^{0.34} \text{ mole}^{-0.34} \text{ hr.}^{-1}$, in agreement with the k' values in Table I.

First-order dependence of reaction 1 on diphenylethylene was established from five experiments having an approximate 10-fold excess of vinyl lithium. A first-order plot in diphenylethylene is illustrated in Figure 3. Values of k' obtained from the slopes of these first-order plots are the same, within experimental variation, as those obtained from the initial slopes of absorbance vs. time curves.

Decomposition of the vinyl lithium-diphenylethylene adduct occurs simultaneous with its formation, as shown in Figure 4. Thus, the final absorbance of the adduct is not exactly equivalent to the original known concentration of DPE. Nevertheless, since the rate of adduct formation is ~ 20 times that of decomposition, addition is essentially complete before appreciable decomposition occurs. The measured maximum absorbance, therefore, is not expected to be more than a few per cent lower than the absorbance of the adduct that would correspond to the initial DPE concentration.

In most experiments it was found that a good estimate of the optical density of the adduct which is equivalent to the original DPE concentration is obtained by extrapolating the slope of the formation curve and that

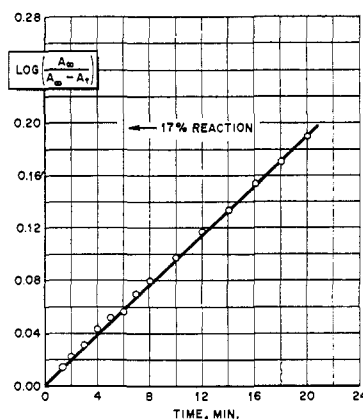


Figure 3. First-order plot in DPE.

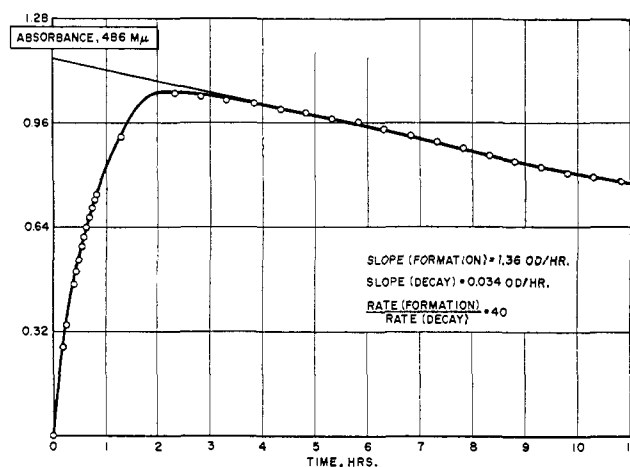


Figure 4. Full reaction curve for $\text{ViLi} + \text{DPE} \rightarrow \text{adduct} \rightarrow \text{decomposes}$.

of the decomposition curve, the intersection being a measure of the maximum optical density that would be attained in the absence of decomposition. The validity of this procedure was established by assuming that formation and decomposition can be treated as two consecutive first-order processes¹³ from which the concentration of adduct at zero time (*i.e.*, before decomposition) may be estimated. Although this calculation requires the assumption of an absorbance maxima, a poor choice will result in the first calculated A_{max} being different from the assumed A_{max} . The procedure can be repeated until the assumed value is in agreement with the calculated value. Absorbance maxima calculated in this manner agreed with those obtained by the extrapolation procedure, within a few per cent. Possible small variations in the value of A_{∞} can cause only small changes in the slope of the first-order plots.

Decomposition of the adduct is identical in a completely sealed apparatus.¹⁴ The rate of decomposition appears to correlate with the amount of excess vinyl lithium in that decomposition is more rapid the larger the excess of vinyl lithium.

The average molar absorptivity of 1,1-diphenyl-3-

(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153.

(14) The adducts formed between *n*-butyllithium or methyl lithium and DPE also undergo decomposition, but at appreciably slower rates.

butyllithium at $486 \text{ m}\mu$ is 3.0×10^4 , calculated using the extrapolated absorbance maxima. This is in good agreement with that obtained for triphenylmethylithium² (3.3×10^4) in which decomposition is not a problem.

Any inaccuracy in the extinction coefficient will appear in the values for k' listed in Table I, but the extinction coefficient has no effect on the slope of Figure 2 and, thus, cannot alter the conclusion that vinylithium is associated in THF solutions.

Discussion

The fractional kinetic order of vinylithium for addition to DPE is evidence that vinylithium is associated in THF solution. The kinetics require that the associated vinylithium is in equilibrium with a more reactive, less associated form.⁴ The one-third order does not require the higher aggregates to be trimers but shows that the less associated, more reactive form is one-third the size of the larger aggregates. By analogy with the findings for *n*-butyllithium, it is likely that the reactive vinylithium species is monomer, and the aggregates are trimers; *i.e.*, $(\text{ViLi})_3 \rightleftharpoons 3\text{ViLi}$.

n-Butyllithium is apparently hexameric in benzene solution over a wide range of concentration, *i.e.*, 10^{-4} to 3 M . There is no indication of the average aggregate size changing with concentration. In contrast, the reactivity behavior of lithium cyclohexylamide in cyclohexylamine indicates an effective aggregate size which depends on concentration over a much smaller range.¹⁵ For example, kinetic orders vary from near first order at $5 \times 10^{-3} \text{ M}$ to near zero order at $5 \times 10^{-1} \text{ M}$.¹⁵ Vinylithium in THF shows no indication of a

(15) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962).

change in effective aggregate size over this same concentration range.

The association of vinylithium in THF, contrasted with the monomeric nature of polystyryllithium⁸ and polyisoprenyllithium⁹ in THF, as well as the general indication of clustering in hydrocarbon solution, illustrates that the solution behavior of organolithium compounds is both structure- and solvent-dependent.

Presumably, the excess negative charge of the vinylithium ion pair is primarily localized in a carbon σ -orbital. The expected high local-charge density is possibly a factor favoring association. A spreading of the excess negative charge *via* delocalization, *e.g.*, in polystyryllithium and polyisoprenyllithium, might be expected to reduce the dipolar attractive forces and favor solvation of the incipient lithium cation.

Rate constants reported for the reaction of DPE with two other organolithium compounds can be compared with that for vinylithium. The second-order rate constant for the addition of DPE to polystyrylsodium in THF¹⁶ is $1.3 \times 10^6 \text{ moles l.}^{-1} \text{ hr.}^{-1}$. In benzene solution k' for addition of *n*-butyllithium to DPE¹⁷ is $9 \times 10^{-2} \text{ mole}^{0.18} \text{ l.}^{-0.18} \text{ hr.}^{-1}$.

Similar kinetic measurements show that methylithium is also associated in THF solution.¹⁸ The association behavior of other organolithium reagents in both olefin addition and metalation reactions in THF solution is being investigated.

Acknowledgment. The authors are grateful to Dr. Peter West and Miss Mary A. Doran of this laboratory for helpful discussions.

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(18) P. West and R. Waack, to be published.

Infrared and Raman Spectra of CF_2N_2 . Evidence for a Diazirine Structure

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The infrared spectrum of CF_2N_2 has been obtained from 4000 to 250 cm.^{-1} , and the Raman spectrum from 2700 to 100 cm.^{-1} . Eight prominent bands in the infrared, 1563, 1282, 805, 502, 1248, 481, 1091, and 544 cm.^{-1} , along with a prominent band in the Raman at 451 cm.^{-1} , have been assigned as fundamentals. The spectra are interpreted as evidence for the cyclic diazirine structure rather than the linear diazomethane structure.

Introduction

This study of the vibrational spectrum of CF_2N_2 was initiated shortly after the compound was first

synthesized; our objective was to establish the structure and to make a vibrational assignment. The hydrocarbon analog, CH_2N_2 , exists in two isomeric forms. Diazomethane which has long been known has a linear structure.² The other isomer, diazirine, has only recently been prepared^{3,4} and shown spectroscopically to have a cyclic structure.^{5,6}

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(2) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," translated by H. E. Nursten, Interscience Publishers, Inc., New York, N. Y., 1961.

(3) E. Schmitz and R. Ohme, *Tetrahedron Letters*, 612 (1961).

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(5) L. Pierce and V. Dobyns, *ibid.*, **84**, 2651 (1962).

(6) R. Ettinger, *J. Chem. Phys.*, **40**, 1693 (1964).

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