Reactivities of Organolithium Compounds in Tetrahydrofuran. I. As Vinyl Polymerization Initiators

Richard Waack and Mary A. Doran

Eastern Research Laboratory, The Dow Chemical Company, Wayland, Massachusetts 01778

Received January 19, 1967

Relative reactivities of 13 structurally different organolithium compounds were determined in tetrahydrofuran solution by a polymerization method in which initiation competes with propagation. Reactivities decrease in the order alkyl > benzyl > allyl > phenyl > vinyl > triphenylmethyl, which shows the effective reactivity order by structure type to be alkyl > charge delocalized > sp^2 hybridized. The order of the reactivity series does not change with changes in reaction conditions. The reactivity behavior of mixed initiators (*i.e.*, an active and an inactive) is essentially that of the most reactive initiator. Variation of polymer molecular weight with polymerization temperature indicates that over-all activation energies for initiation are larger than for propagation and that the difference is larger the less reactive the initiator.

There is very little information relating to the effect of structure on the reactivity of organolithium compounds. This work illustrates the effective relative reactivities of structurally different organolithium compounds as initiators for the polymerization of styrene in tetrahydrofuran (THF) solution.[1] Relative reactivities were determined under conditions such that initiation effectively competes with propagation throughout the polymerization. This competitive scheme circumvents complications from the extremely fast absolute rates of these reactions in THF solution.

There is no prior work relating structure of organolithium reagents to activity as *polymerization initiators* in THF solution. Reactivity information is available for several organolithium reagents from rates of reaction with THF[2] or diethyl ether,[3] from product yields resulting from the metalation of dibenzofuran in THF,[4] and from kinetic studies of the rates of metalation of triphenylmethane in THF.[5] Among these studies differences in the structure reactivity order are found. Thus, a variation in relative reactivity with substrate is indicated. For example, compare metalation[5] reactivities with those reported here for olefin addition. Competition between an alkyl- and aryllithium reagent for reaction with insufficient Michler's ketone in benzene solution showed the latter to be more reactive than the former[6] toward this substrate, which contrasts the behavior reported here.

It is significant that the structure-reactivity behavior found for organosodium compounds as initiators of styrene polymerization[7] or addition to 1,1-diphenylethylene,[8] although done as heterogeneous reactions in hydrocarbon solution, is virtually identical with that found in this study.

In an aprotic solvent, the gross feature of an anionic polymerization can be described by two kinetic steps, *viz.*, initiation, $\text{RLi} + \text{St} \rightarrow \text{RStLi}$, and propagation, $\text{RStLi} + n\text{St} \rightarrow \text{RSt}_n\text{StLi}$. There is no spontaneous termination and polymerization continues until all the monomer is consumed. Because termination is absent and initiator is present in excess throughout, the degree of polymerization (DP) of the polymer is determined by the ratio of the over-all rate of propagation to that of initiation. Therefore, the number-average molecular weight of the polymer produced is a measure of the effective reactivity of the initiator compared with that of the propagating anionic polymer species, styryllithium. A further consideration is that propagation rate is independent of the nature of the excess initiator, which is supported by experiments using mixtures of initiators. The *order* of the reactivity series is found to be independent of the experimental conditions. The magnitudes of the relative values are not, however, independent of conditions.

Experimental Section

Standard polymerizations were done in THF solution at 20°. Morton creased flasks (100-ml volume) were used. The flasks were alternately pumped to high vacuum and flushed with argon three times before being pressurized with argon. Reactions were stirred magnetically using glass enclosed bars. The organolithium compounds were added *via* gas-tight syringes and made up in THF to 0.25 *M* solution of 6-ml total volume. Styrene monomer (2 ml) sufficient to give an initial monomer to initiator molar ratio (M:I)[9] of 11.5 was then added rapidly (approximately 0.2 cc/sec). The polymerizations were thermostated using a water bath. The reactions instantly take on the deep red color of styryllithium. Polymerization usually was essentially complete as soon as monomer addition was completed. Standard practice was to stir the reaction for 10 min and then terminate with ethanol.

In representative cases analysis for the amount of unreacted initiator showed it to be in agreement with that anticipated from the molecular weight of the recovered polymer. These residual initiator analyses were done as follows: *n*-butyllithium and phenyllithium by quantitative gas–liquid partition chromatography (glpc) measurement of butane and benzene after quenching, vinyllithium by total gas evolution after quenching. The poorest agreement occurred with *n*-butyllithium where $\sim$12% less butane was found than anticipated from the polymer DP. Reaction of the butyllithium with THF during the 10-min period probably contributes to this difference.

The polymer solutions were filtered, made cloudy with methanol, precipitated in methanol and reprecipitated from 2-butanone solution into methanol, and dried *in vacuo* at 40°. Polymer yields were essentially quantitative. Polymer solution viscosities were determined in toluene at 25° using Ubbelohde viscometers having solvent flow times of $\sim$100 sec. Plots of reduced and inherent viscosity *vs.* concentration were extrapolated to zero concentration. Intersection of the two plots defines the intrinsic viscosity.[10] These values were converted to polymer

---

[1] Preliminary report: R. Waack and M. A. Doran, *Polymer*, **2**, 365 (1961). Presented in part at the National Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966, Polymer Preprints, Vol. 7, 1966, p 56.

[2] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

[3] H. Gilman, A. H. Haubein, and H. Hartzfeld, *ibid.*, **19**, 1034 (1954).

[4] H. Gilman and H. A. McNinch, *ibid.*, **27**, 1889 (1962).

[5] R. Waack and P. West, *J. Am. Chem. Soc.*, **86**, 4494 (1964).

[6] C. G. Swain and L. Kent, *ibid.*, **72**, 518 (1950).

[7] A. A. Morton and E. Grovenstein, Jr., *ibid.*, **74**, 5434 (1952).

[8] A. A. Morton and E. J. Lanpher, *J. Polymer Sci.*, **44**, 239 (1960).

[9] To maintain the condition of competition between initiator and propagating polystyryllithium for monomer throughout the polymerization, it is necessary to keep the ratio of total added monomer to total initiator small.

[10] F. W. Billmeyer, Jr., "Textbook of Polymer Science," Interscience Publishers, Inc., New York, N. Y., 1962, pp 80–81.

molecular weights using the relationship of Mayo, *et al.*,[11] which relates intrinsic viscosity to osmotic molecular weights of unfractionated polymers. Good agreement between molecular weights measured by solution viscosities and those determined by three absolute number-average molecular weight methods is illustrated for the lower molecular weight polymers in Table I.

TABLE I

COMPARISON OF POLYMER MOLECULAR WEIGHTS DETERMINED BY VISCOMETRIC AND ABSOLUTE METHODS

Viscosity	Bp elev[a]	Near-infrared spectrum[b]	Osmometer[c]	Initiator
2,450	2,520	...	2,700	n-C_4H_9Li
3,000	2,950	...	...	n-C_4H_9Li
3,200	3,420	...	...	C_2H_5Li
7,000	6,400	...	6,800	$C_6H_5CH_2Li$
7,200	7,040	...	...	Lithium naphthalene
9,900	10,500	10,000	...	$CH_2{=}CHCH_2Li$
11,000	10,500	10,400	10,200	$CH_2{=}CHCH_2Li$
14,000	14,500	12,800	...	$CH_2{=}CHCH_2Li$
21,500	17,500	...	...	$CH_2{=}CHLi$
23,000	17,900	...	...	$CH_2{=}CHLi$

[a] Average of three determinations. These determinations were made at the Analytical Laboratory, The Dow Chemical Co., Midland, Mich. [b] The concentration of vinyl hydrogen was determined in the near-infrared spectrum from the absorption at 1.633 and 1.644 μ of the first overtone of the CH stretching mode (R. F. Goddu, *Anal. Chem.*, 29, 1790 (1957)). Extinction coefficients were based on the absorption of 1-phenyl-3-butene. Molecular weights were calculated assuming one vinyl group per polymer chain. [c] Using Mechrolab osmometer, and extrapolating a plot of $\Delta R/c$ *vs.* c to zero concentration.

THF was distilled under argon from lithium dispersion containing a small amount of benzophenone ketyl or from lithium aluminum hydride. Styrene monomer was vacuum distilled from calcium hydride. All reagents were handled *via* Hamilton gas-tight syringes.

n-Butyllithium, *sec*-butyllithium, and *t*-butyllithium were obtained from Foote Mineral Corp. and Lithium Corp. of America as hydrocarbon solutions. Ethyllithium was obtained as a benzene solution from Orgmet, Hempstead, N. H. Salt-free phenyllithium (containing ~0.25% chloride ion) was obtained from Lithium Corp. of America in diethyl ether–benzene solution. Phenyllithium was prepared from diphenylmercury and lithium in THF or diethyl ether. Phenyllithium containing stoichiometric LiX was prepared from bromobenzene or chlorobenzene and lithium in ether or THF solutions.[12] Vinyllithium[13] and allyllithium[14] were prepared in *n*-hexane from the corresponding tetrasubstituted tin compounds *via* transmetalation with *n*-butyllithium (using 1:2 molar ratio). The hexane-insoluble organolithium was washed three times with hexane before dissolving in dry THF. α-Methylbenzyllithium and crotyllithium were prepared from the corresponding triphenyltin compounds[15] *via* transmetalation with phenyllithium in diethyl ether. The reaction was chilled after 2 hr to precipitate the tetraphenyltin and filtered. Benzyllithium was prepared from tribenzyltin chloride and phenyllithium in diethyl ether, and from dibenzylmercury and lithium in THF. *p*-Tolyllithium was prepared from di-*p*-tolylmercury and lithium in THF or ether. Methyl lithium was prepared from dimethylmercury and lithium in THF or ether. In these preparations recovery of tetraphenyltin or mercury was 95–100% of theoretical. Triphenylmethyllithium was prepared from triphenylchloromethane and lithium in THF. Concentrations and characterizations of the organolithium reagents were done by acid titration of total alkali ultraviolet absorption spectrum, carbonation, or manometric analysis when a volatile gas was formed on hydrolysis, as described previously.[16]

Results and Discussion

Relative reactivities of 13 organolithium compounds, as indicated by the polymer molecular weights, are given in Table II in the order of decreasing reactivity. The magnitude of the molecular weight of the styrene polymers is inversely related to the activity of the respective organolithium reagents as polymerization initiators. Based on structural similarities, these reagents are considered as representative of four structural types: (a) alkyl, (b) resonance stabilized, (c) sp^2 hybridized nondelocalized, and (d) resonance stabilized sterically hindered. Each structure class is self-consistent in its reactivity.

TABLE II

"STANDARD POLYMERIZATIONS" OF STYRENE IN TETRAHYDROFURAN SOLUTION AT 20°

Organolithium	Mol wt[a] (temp, °C)
t-Butyl	3,200[b] (−66)
	3,200 (−40)
sec-Butyl	3,500[b] (−69)
Ethyl	3,500
n-Butyl	3,600
α-Methylbenzyl	3,700
Crotyl	6,500
Benzyl	6,700
Allyl	9,600
p-Tolyl	9,900
Phenyl[c]	12,000
Phenyl[d] (LiX)	24,000 (LiCl)
	22,000 (LiBr)
Methyl	19,000
Vinyl	23,000
Triphenylmethyl[e]	66,000
Triphenylmethylsodium	53,000
Lithium naphthalene	6,000

[a] Average values. [b] At higher temperatures there is rapid reaction with THF. [c] Salt free. [d] Contains equimolar lithium halide (see ref 12). [e] Contains equimolar LiCl. Lithium halides are indicated to have little effect on the reactivity of such resonance stabilized species.[12]

The alkyllithiums, represented by the isomeric butyllithiums and ethyllithium, are the most reactive initiators. These species are so active as polymerization initiators in THF solution that only small differences were obtained in their reactivity under these experimental conditions. *t*-Butyllithium and *sec*-butyllithium react rapidly with the THF solvent at 20°; so reliable evaluation at this temperature was not possible. Comparative reactivities obtained at lower temperature are probably representative owing to the temperature-independent behavior of these initiators. Temperature dependence will be discussed in a following section. The high reactivity found for *t*-butyllithium is in agreement with its ability to add ethylene to form a primary lithium compound[17] (which then does not react further with ethylene) and is in accord with its propensity to react with the solvent. Relative rates of alkylation of naphthalene in *hydrocarbon* solution,

---

[11] F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

[12] The presence of lithium halides decreases the reactivity of phenyllithium: R. Waack and M. A. Doran, *Chem. Ind.* (London), 496 (1964).

[13] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

[14] D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

[15] Kindly supplied to us by Dr. F. C. Leavitt and Priscilla A. Carney, Eastern Research Laboratory, The Dow Chemical Co., Wayland, Mass.

[16] R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963); *J. Phys. Chem.*, **67**, 148 (1963).

[17] P. D. Bartlett, M. Stiles, and S. Friedman, *J. Am. Chem. Soc.*, **75**, 1771 (1953).

which involves addition to a double bond followed by elimination, are reported to decrease in the order tertiary > secondary > normal,[18] in accord with the behavior found here in THF solution. Rates of initiation of diene polymerization in hydrocarbon solution indicate relative reactivities of the isomeric butyllithiums decrease in the order secondary ~ tertiary > normal,[19,20] whereas with styrene *sec*-butyllithium was the most reactive and *t*-butyllithium the least reactive.[20]

The smallest member of the alkyl series, methyllithium, is shown to be comparatively unreactive. Although this is in agreement with its behavior in other reactions,[2,5] the substantially lower reactivity of methyllithium is not expected to be an intrinsic property of methyl *vs.* other alkyl groups. More likely, it is a consequence of the physical nature of methyllithium in solution as discussed in a following section. The different nature of methyllithium is also indicated by its insolubility in hydrocarbon solution, whereas the other alkyllithiums are substantially more soluble.

After the alkyls, the next most reactive structure type is the resonance stabilized species such as benzyllithium and allyllithium. Because these species are considered to have enhanced thermodynamic stability as a result of charge delocalization,[21] and because relative rates of proton exchange are found to relate directly to the thermodynamic stabilities of the respective "carbanions,"[21,22] this high level of kinetic activity for resonance stabilized organolithium reagents is significant. It illustrates that relative kinetic activity does not follow relative thermodynamic behaviors. Studies of rates of metalation[5] showed a correspondingly high reactivity for benzyllithium and allyllithium. The analogous sodium derivatives also show a correspondingly high reactivity in olefin addition reactions.[7,8]

Organolithium compounds in which the C–Li bond is presumed to have predominantly sp^2 character are found to be the least reactive type of the simple organolithium compounds. Consideration of only relative basicities[23] would predict these species to be less reactive than the alkyls, but more reactive than those species in which there is resonance stabilization. It is noteworthy that the lower kinetic activity of vinyllithium compared to phenyllithium is in accord with the relative carbanion stabilities determined by halogen lithium interconversion equilibria.[24]

Triphenylmethyllithium which is highly resonance stabilized and presumably sterically hindered is the least reactive of these organolithium species. Inactivity of the triphenylmethyl moiety, relative to styryl, is illustrated by a previous report. Similarly only high molecular weight polymer could be isolated and little of the triphenylmethylsodium was consumed[25] when it was used as an initiator for styrene polymerization in ether solution.

Substitution of methyl for H in a position such that the perturbation is transmitted to the carbon–lithium bond, makes the lithium reagent a more reactive initiator, *i.e.*, compare α-methylbenzyl with benzyl, crotyl with allyl, and *p*-tolyl with phenyl. Replacement of H by methyl is known to decrease acid strength of a hydrocarbon; *i.e.*, alkyl substituents increase "carbanion" base strength.[22] Equilibrium studies showed phenyllithium to be more stable than *p*-tolyllithium.[26] The change in reactivity induced by methyl in the above organolithiums is analogous. The inference is that within a structure class relative organolithium reactivity correlates with relative "carbanion" thermodynamic base strength. Deviation from this behavior is likely due to differences in solution behavior of the various structure classes, as discussed in a following section.

Alkyl substitution on a carbon removed from the reactive carbon–lithium bond, providing it is neither part of a conjugated system nor can its effect be transmitted by polarizable π electrons, induces little change in reactivity other than what could be attributed to steric factors, *e.g.*, compare ethyl *vs.* *n*-butyl. In hydrocarbon solution ethyllithium was also shown to be slightly more reactive than *n*-butyllithium as an initiator for polymerization of styrene.[27]

Initiation by triphenylmethylsodium, relative to propagation by polystyrylsodium, is indicated to be enhanced compared to that of the corresponding lithium derivative. Solvent and counter ion effects on reactivity will presumably differ depending on the structure of the organic entity.

α-Methylbenzyllithium is virtually identical structurally with the propagating polystyryllithium. That polymer of DP higher than the theoretical monomer to initiator ratio is produced with this initiator could indicate a higher reactivity for the polymeric species than for its low molecular weight counterpart. An indication that propagation is a favored reaction is that in diethyl ether solution even using extreme conditions least favorable to propagation only a small amount of product characteristic of the *n*-butyllithium styrene monoadduct could be obtained.[28] On the other hand, the formation of polymer with α-methylbenzyllithium and also the alkyllithiums could to some extent be a consequence of inhomogeneity of mixing. Conceivably, in these fast reactions an initiator molecule entering a styrene-rich area could cause polymerization of the styrene more rapidly than it is dispersed. Use of rapid high-speed mechanical stirring, however, produced polymer of molecular weight essentially unchanged from that obtained using magnetic stirring, with both a representative "active" (*n*-butyllithium) and "inactive" (phenyllithium) initiator.

It is interesting that under these conditions the reactivity of the radical anion lithium naphthalene is between that of the alkyllithiums and the resonance-stabilized species.

---

[18] J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, No. 12, 613 (1964).

[19] I. Kuntz, *J. Polymer Sci.*, **2A**, 2827 (1964).

[20] H. L. Hsieh, *ibid.*, **3A**, 163 (1965).

[21] Thermodynamic stability of the "carbanion" (ion pair) is directly related to the acidity of the corresponding hydrocarbon. Relative acidities are toluene > benzene ≫ alkyl; see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 19, 20–31, and 49–55.

[22] A. O. Shatenshtein, *Advan. Phys. Org. Chem.*, 1, 187 (1963); A. Streitwieser, Jr., and D. E. Van Sickle, *J. Am. Chem. Soc.*, **84**, 249 (1962).

[23] Increasing s character of the R_2CH bond results in increased acidity, hence weaker basicity for the conjugate base, R_2CLi: H. A. Bent, *Chem. Rev.*, **61**, 275 (1961); G. L. Closs, and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965); ref 20, pp 48–50.

[24] D. F. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

[25] K. Ziegler, *Ann.*, **567**, 43 (1950).

[26] H. J. S. Winkler and H. Winkler, *J. Am. Chem. Soc.*, **88**, 964 (1966).

[27] G. C. East, P. F. Lynch, and D. Margerison, *Polymer*, **4**, 139 (1963).

[28] R. C. P. Cubbon and D. Margerison, *Proc. Chem. Soc.*, 146 (1960).

Effect of Reaction Variables on Reactivity Order.—It is important to establish that the reactivity order obtained in these competitive experiments is not only valid under the standard reaction conditions. Studies of the effect of changing[29] molar ratio monomer to initiator (from 6 to 40), initiator concentration (from 0.75 to 0.05 *M*), monomer concentration (factor of 10), order of mixing initiator and styrene, and rate of monomer addition established that the *order* of the reactivity series does not change with these changes of the experimental conditions. Species of similar structure type responded similarly to a change in reaction conditions, further illustrating the correspondence in their reactivity behaviors. The reactivity *order* is, thus, shown not to be sensitive to the experimental conditions. Magnitudes of the relative reactivities, however, are variable with certain of the experimental conditions.

For three representative initiators the reactivity *order* was found to be the same in diethyl ether as in THF. Appreciably lower polymer molecular weights were obtained in diethyl ether compared to those obtained in THF under the same conditions. Thus, initiation rate is increased relative to the propagation rate in the former solvent compared to the behavior in the latter. Enhancement of initiation rate relative to propagation in solvents of decreasing polarity was also observed in similar systems.[30]

The comparative reactivity of *n*-butyllithium and phenyllithium was found to be approximately the same for the monomers *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, *t*-butylstyrene, and isoprene, thus, indicating the order of the reactivity series is independent of the nature of the monomer. Degrees of polymerization obtained with isoprene under the standard conditions were one-seventh to one-tenth those obtained with styrene indicating that for isoprene initiation is favored relative to propagation, compared to the behavior of styrene.

Effect of Mixed Initiators.—One of the assumptions inherent in this method of determining relative reactivities is that the rate of propagation is independent of the nature of the initiating organolithium species in solution. Results of experiments using mixtures of two initiators, an "active one" and an "inactive one," are in support of this assumption. The molecular weight of the polymer produced under these conditions is essentially that which would be formed by the most active initiator independently. Apparently, the less active initiator is unable to compete and its presence produces no marked effect on the comparative propagation rate.

Temperature Dependence.—Polymerizations initiated by the more active initiators are independent or only slightly temperature dependent, whereas polymerizations initiated by the less active initiators are appreciably temperature dependent. In these competitive polymerizations under aprotic conditions, initiation competes with propagation until the monomer is exhausted. Average polymer DP is thus given by the ratio of the over-all rate of propagation ($R_p = k_p[M^*][St]$) to the over-all rate of initiation ($R_i = k_i[I]^n[St]$) where n is indicated to be a fractional value for some initiators. By substituting for the rate constants the temperature dependence of the polymer DP can be expressed in the following manner

$$\mathrm{DP} = \frac{[\mathrm{M}^*]}{[\mathrm{I}_0 - \mathrm{M}^*]^n} \frac{A_p}{A_i} e^{-(E_p - E_i)/RT}$$

where [M*] represents polystyryllithium and is presumed equal to the amount of initiator [I] consumed. Plots of $\log \mathrm{DP} + \log_0 [\mathrm{I}_0/(\mathrm{M}^* - 1)]$ *vs.* $1/T$ are linear.[31] Slopes of these plots should relate to the differences between the effective activation energy for propagation and the activation energies for initiation by the various organolithium species. Temperature coefficient values obtained from these experiments are listed in Table III.

TABLE III

TEMPERATURE COEFFICIENTS FOR ORGANOLITHIUM INITIATED STYRENE POLYMERIZATION IN TETRAHYDROFURAN SOLUTION

Organolithium initiator	Temp coefficient[a] $[E_i - E_p]$, cal
α-Methylbenzyl	Temp independent
n-Butyl	270
Benzyl	830
Allyl	1290
p-Tolyl	5500
Phenyl	7500
Vinyl	9000
Triphenylmethyl	8700

[a] Temperature range −78 to 30°.

The effect of temperature change on these competitive polymerizations is to cause an increase in polymer molecular weight with a decrease in temperature, which shows that the propagation reaction is less temperature dependent than is the initiation reaction. To the extent that initiation and propagation are truly competitive and that the excess initiator does not perturb the propagation reaction, these temperature coefficients should be equivalent to the relative activation energy differences between initiation and propagation for the different initiators. However, to the extent that the polymer molecular weights are influenced by mixing of the reactants, the $E_i - E_p$ obtained would be expected to be less than the true value. The $E_i - E_p$ values indicate that the less reactive initiators have higher activation energies for initiation than do the more reactive species. The order of the reactivity series is independent of temperature. A greater spread in the measured reactivities occurs with decreasing temperature. The reactivity of α-methylbenzyllithium relative to polystyryllithium is independent of temperature. We interpret this as indicating that reactivity behavior of this reagent is analogous to that of polystyryllithium. The molecular weight of polymers initiated by *t*-butyllithium and *sec*-butyllithium were also independent of temperature, below 0°; at higher temperatures these reagents react too rapidly with the THF solvent to obtain a meaningful result.

There are no reports of activation energies for *initiation* of vinyl polymerizations by organoalkali metal reagents in THF solution. Analogous to the

---

(29) All other experimental conditions, except that being tested, were "standard."

(30) F. W. Brower and H. W. McCormick, *J. Polymer Sci.*, **1A**, 1749 (1963).

(31) Calculated for $n = 1$. The value of n has negligible effect on the plot.

finding here, the activation energy for initiation of styrene by n-butyllithium in benzene solution is reported to be greater than that for propagation.[32] The activation energy for initiation of isoprene by n-butyllithium in diethyl ether is also reported to be greater than that for propagation;[33] however, the situation is reversed in heptane.[34]

The organolithium reagents, owing to the relatively high concentration used in these experiments, no doubt exist as ion pairs or clusters of ion pairs in which the incipient lithium cation is expected to be strongly solvated. The transition state for olefin addition under these conditions is presumed to be of the four-center type involving stretching of the carbon–lithium bond while simultaneously forming new carbon–carbon and carbon–lithium bonds.

It is known that organolithium compounds are associated in hydrocarbon solution[35] and this has been shown to affect the kinetics of their reactions.[32,36] Kinetic behaviors of some organolithium compounds in THF solution[37,38] suggest the alkyl and sp^2-type species may be aggregated in this solvent, whereas other species such as benzyl and allyl are indicated to be monomeric.[38] Aggregation of the organolithium compounds in THF solution is thus indicated to differ for different structure types. Assuming that the aggregate must be disrupted prior to or during the reaction, both the extent and energy of clustering would be a critical factor influencing the relative reactivities of these species.

The relative reactivities determined in this study, thus, represent *effective* reactivities characteristic of the respective organolithium species. Equating the measured reactivities with inherent reactivities characteristic of the organic moiety, with the exclusion of other structure dependent variables, must take possible differences in solution properties into account. This will require detailed kinetic and solution property studies, which are in progress.

Registry No.—t-Butyllithium, 594-19-4; *sec*-butyllithium, 598-30-1; ethyllithium, 811-49-4; n-butyllithium, 109-72-8; α-methylbenzyllithium, 13950-05-5; crotyllithium, 13950-06-6; benzyllithium, 766-04-1; allyllithium, 3052-45-7; p-tolyllithium, 2417-95-0; yllithium, 591-51-5; phenyllithium· LiCl, 13950-09-9; phenyllithium· LiBr, 13950-10-2; methyllithium, 917-54-4; vinyllithium, 917-57-7; triphenylmethyllithium, 13950-11-3; THF, 109-99-9.

---

[32] D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960).

[33] H. Sinn and F. Banderman, IUPAC Meeting, Prague, 1965, Preprints, p 575.

[34] H. Sinn, C. Lundborg, and O. L. Onsager, *Macromol. Chem.*, **70**, 222 (1963).

[35] D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2053 (1963); T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).

[36] K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **35**, 259 (1959); A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961); D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960). Other references cited in ref 37 and 38.

[37] R. Waack and P. E. Stevenson, *J. Am. Chem. Soc.*, **87**, 1183 (1965).

[38] R. Waack and P. West, *J. Organometal. Chem.* (Amsterdam), **5**, 188 (1966).

Epoxidation of Alkylidenecyanoacetic Esters with Hydrogen Peroxide and Related Reactions[1]

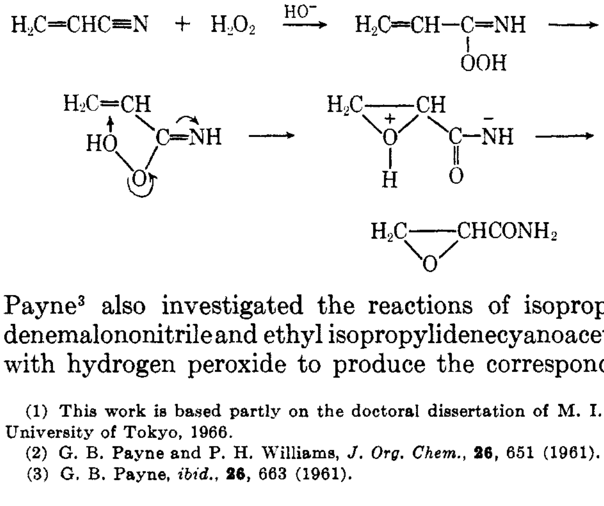
MINORU IGARASHI AND HIROSHI MIDORIKAWA

The Institute of Physical and Chemical Research, Komagome, Bunkyo-ku, Tokyo, Japan

Received February 23, 1967

The reaction mechanism of alkylidenecyanoacetic esters with hydrogen peroxide in the presence of sodium tungstate or trisodium phosphate is discussed. It is concluded that the first step is the nucleophilic attack of the pertungstate anion (or perhydroxyl anion in the case of phosphate catalysis) on the double bond to give the corresponding epoxy nitrile, hydrolysis of which with alkaline hydrogen peroxide gives the epoxy amide. The fact that an epoxy nitrile intermediate was detected supports this view.

Payne and Williams[2] studied the base-catalyzed reaction of acrylonitrile with hydrogen peroxide to give glycidamide and proposed the mechanism shown in eq 1.



(1)

Payne[3] also investigated the reactions of isopropylidenemalononitrile and ethyl isopropylidenecyanoacetate with hydrogen peroxide to produce the corresponding epoxy amides (along with some epoxy nitriles). It seems, however, that the mechanism for the reaction of basic hydrogen peroxide with ethyl isopropylidenecyanoacetate was not extensively studied.

In the preceding paper,[4] we studied the synthesis of the epoxy amides II from ethyl alkylidenecyanoacetates I and hydrogen peroxide in the presence of sodium tungstate or trisodium phosphate. In continuation, the mechanism of the reaction has now been studied.

Tungstate Catalysis.—Methyl 2-cyano-3-methyl-2-butenoate (Ia) reacted at 70° (1 hr) with 30% hydrogen peroxide in the presence of sodium tungstate, to give methyl 2-carbamoyl-2,3-epoxy-3-methylbutanoate (IIa) along with some methyl 2-cyano-2,3-epoxy-3-methylbutanoate (IIIa) and methyl 2-carbamoyl-3-methyl-2-butenoate (IVa). Three possible reaction courses are visualized as shown in Scheme I.

---

[1] This work is based partly on the doctoral dissertation of M. I., The University of Tokyo, 1966.

[2] G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961).

[3] G. B. Payne, *ibid.*, **26**, 663 (1961).

[4] M. Igarashi and H. Midorikawa, *ibid.*, **28**, 3088 (1963).