# The Addition to and Alkylation of Naphthalene by *t*-Butyllithium. Kinetics and Mechanism

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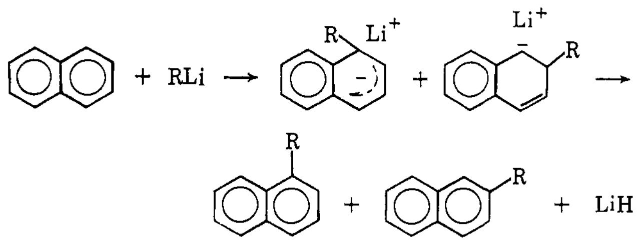
**Abstract**: The reaction of *t*-butyllithium and naphthalene in decalin solution to yield addition and alkylation products was subjected to a kinetic investigation. The total reaction was found to obey a pseudo-first-order kinetic dependence. Initial rate studies, however, demonstrated that the experimental rate equation for initial conditions was: $\text{rate}_i = k'(\text{ArH})(\text{RLi}/4)^{1/2}$, where $k' = k(\text{ROLi})^{-1/4}$. From the kinetic behavior and activation parameters it was concluded that an intermediate complex is quantitatively formed prior to the rate-determining addition of *t*-butyllithium to naphthalene.

During a study of reactions of alkyllithium reagents in hydrocarbon solvents, an interesting reaction with aromatic hydrocarbons was observed.[2] The products of this reaction apparently resulted from addition to and alkylation of the aromatic nucleus by the alkyllithium reagent. Metallation of the aromatic compound, which was normally observed with these reactants in polar media,[3] was notably present. Although other investigators had reported alkylations of aromatic compounds by organometallic reagents, these reactions were observed with heteronuclear aromatic compounds,[4] with nonbenzenoid aromatic compounds,[5] or as minor side reactions.[6]

The addition–alkylation reaction for which a complete product analysis had been performed previously[2] consisted of naphthalene and *t*-butyllithium in decalin solution and can be summarized by the following scheme (R = *t*-butyl).



In an effort to define the mechanism of this reaction a kinetic study was performed in which chemically quenched aliquots were analyzed by vapor phase chromatography (vpc).

## Results and Discussions

**Addition–Alkylation Reaction Profiles.** The vpc analyses of water-quenched reaction samples yielded relative measures of the aromatic species present and from these reaction profiles were constructed (Figures 1–4) which displayed the concentrations of the aromatic components as a function of time. Although the addition product was not very soluble in the reaction system, it is believed that representative sampling was accomplished.

A typical reaction profile for a reaction at 100° is shown in Figure 1. Although the profile is consistent with a two-step process involving an intermediate (the addition product), an explanation invoking kinetic *vs.* thermodynamic control could not be excluded. Figure 2 shows the isomeric content of the ultimate product, *t*-butylnaphthalene, as a function of time for this reaction. The slight decrease in the concentration of 2-*t*-butylnaphthalene after attaining a maximum is due to further alkylation of this isomer by unreacted *t*-butyllithium. An induction period in the formation of 1-*t*-butylnaphthalene is also evident in Figure 2 suggesting the presence of an intermediate or a chain process.

The profile shown in Figure 3 was obtained for a similar reaction at 73.5°. The isomer profile (Figure 4) demonstrates that both alkylate isomers experience induction periods at this temperature, and that the induction period for 1-*t*-butylnaphthalene is the longer.

Metallation was shown not to be a significant competitive reaction by quenching samples from a reaction at 100° with methyl iodide. Less than 2% of the total aromatic product was methylnaphthalenes.

**The Addition Product.** As previously noted, the solubility of the addition product was low in the reaction system, 0.030 ± 0.004 *M* at 27.5°. Solubilities at higher temperatures could not be determined due to reaction. The cryoscopic molecular weight of this material was 360 ± 14, theory 192. Apparently the addition product is primarily dimeric in hydrocarbon solution.

From a reaction of the isolated addition product in decalin at 74°, the profile shown in Figure 5 was obtained. It is evident that both naphthalene and 1-*t*-butylnaphthalene are formed from the isolated addition product and, further, that a significant reaction occurred prior to quenching of the first reaction sample. A similar reaction was quenched with deuterium oxide and the

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(1) Taken in part from the Ph.D. thesis of R. L. Eppley, submitted to The Pennsylvania State University, University Park, Pa., 1967.

(2) (a) J. A. Dixon and D. H. Fishman, *J. Am. Chem. Soc.*, **85**, 1356 (1963); (b) J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 613 (1964); (c) D. H. Fishman, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1964.

(3) (a) R. G. Jones and H. Gilman in "Organic Reactions," Vol. VI, Roger Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951; (b) G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960; (c) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) (a) K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930); (b) *Ann.*, **485**, 174 (1931).

(5) (a) K. Hafner and H. Weldes, *ibid.*, **606**, 90 (1957); (b) K. Hafner, H. Pelster, and H. Patzelt, *ibid.*, **650**, 80 (1961); (c) K. Hafner, C. Bernhard, and R. Muller, *ibid.*, **650**, 350 (1961).

(6) D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.*, 861 (1953).

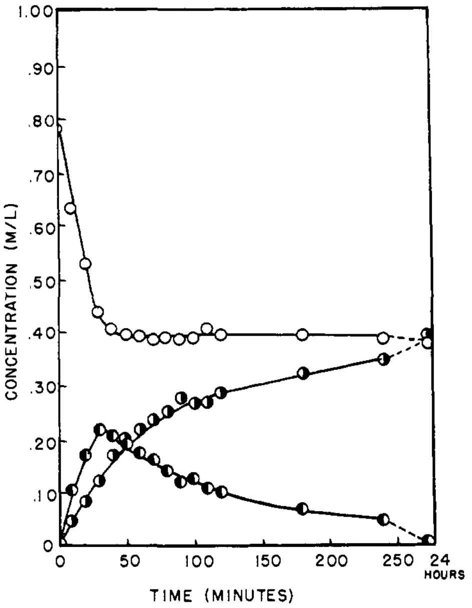

Figure 1. Reaction profile for a total kinetic run at 100°: ○, naphthalene; ◐, addition products; ◑, *t*-butylnaphthalenes; $(RLi)_0 = 0.586\ M$.

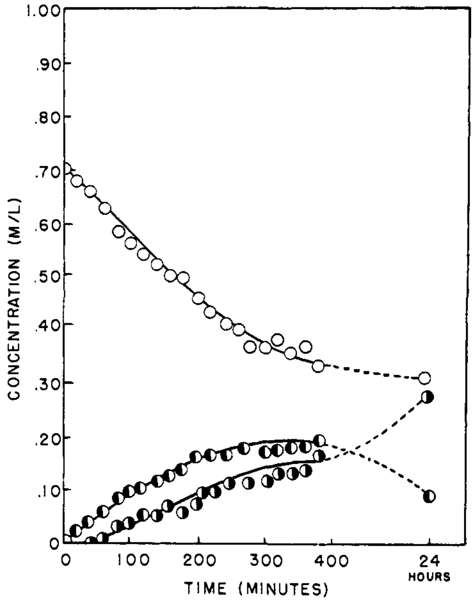

Figure 3. Reaction profile for a total kinetic run at 73.5°: ○, naphthalene; ◐, addition products; ◑, *t*-butylnaphthalenes; $(RLi)_0 = 0.409\ M$.

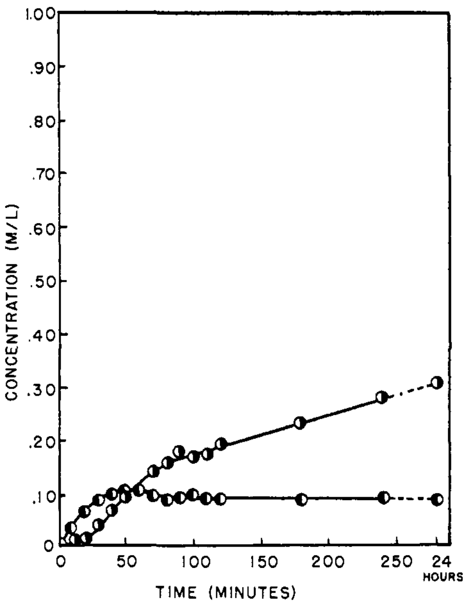

Figure 2. Alkylate isomer profile for a total kinetic run at 100°: ◑, 1-*t*-butylnaphthalene; ◐, 2-*t*-butylnaphthalene.

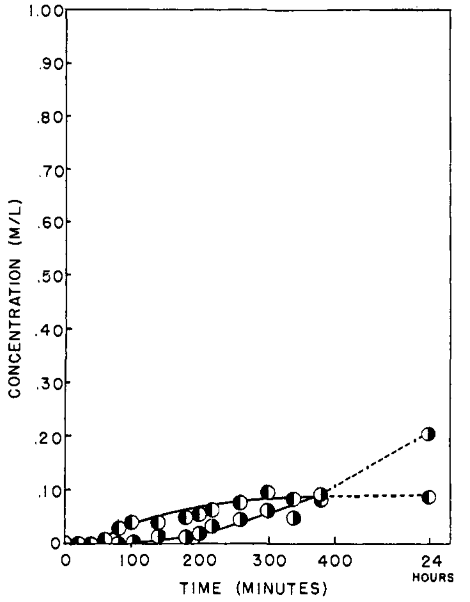

Figure 4. Alkylate isomer profile for a total kinetic run at 73.5°: ◑, 1-*t*-butylnaphthalene; ◐, 2-*t*-butylnaphthalene.

naphthalene isolated. When a 10% solution in $CCl_4$ was analyzed by infrared spectrophotometry, no absorption due to the C–D bond[7] was observed. This indicates that the addition product is in equilibrium with the reactants.

The absence of an induction period in the formation of 1-*t*-butylnaphthalene from isolated addition product (Figure 5) and the presence of an induction period in the complete reaction (Figure 4) were considered to demonstrate the intermediacy of the isolated addition product in the formation of 1-*t*-butylnaphthalene. Intermediacy of this addition product was also supported by comparison of the values calculated for the rates of formation of 1-*t*-butylnaphthalene from isolated addition product and from starting materials at a time of similar apparent concentration of addition product. These values are shown in Table I.

**Table I.** Kinetic Test of Intermediacy of Isolated Addition Product

| Reaction | Apparent concn of addition product, *M* | Rate of formation of 1-*t*-butylnaphthalene, *M* min$^{-1}$ |
|---|---|---|
| Addition product to alkylate at 74° | 0.109 | $3.85 \times 10^{-4}$ |
| Addition product to alkylate at 74° | 0.136 | $5.00 \times 10^{-4}$ |
| Total reaction at 73.5° | 0.140 (time = 190 min) | $2.63 \times 10^{-4}$ |

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[7] J. A. Dixon and R. W. Schiessler, *J. Phys. Chem.*, **58**, 430 (1954).

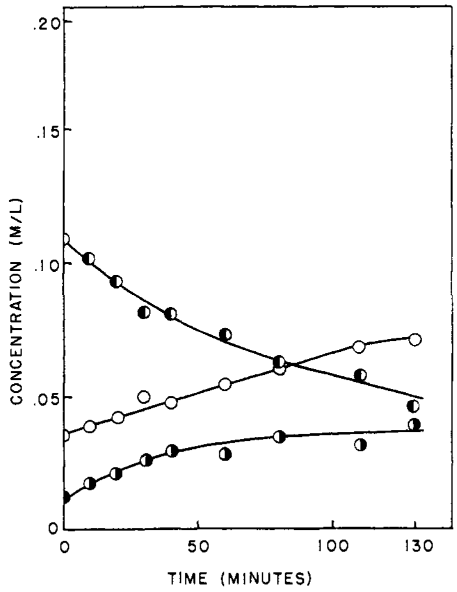

Figure 5. Reaction profile for kinetic test of intermediacy of isolable addition product at 74.0°: ◐, addition product; ○, naphthalene; ◑, 1-*t*-butylnaphthalene.

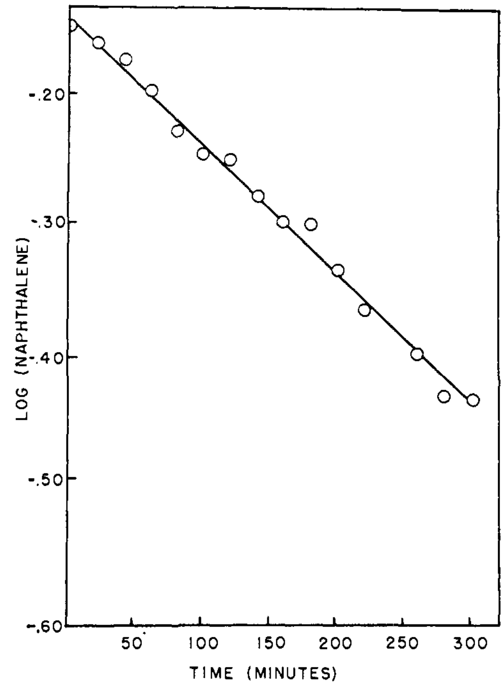

Figure 6. Pseudo-first-order plot for a total kinetic run at 73.5°; reaction profile in Figure 3.

Although the rates of formation of alkylaromatic from the initial reactants and from the presumed intermediate are not identical they are of the same order of magnitude. In heterogeneous systems, variables other than concentration, *e.g.*, particle size, rate of stirring, etc., affect the rate of reaction, and therefore the difference in the rates is not considered significant in this case.

Inasmuch as the reaction profile for 2-*t*-butylnaphthalene also displayed an induction period (Figure 4), it was believed that this isomer was also preceded by an intermediate addition product. Failure to isolate such an intermediate was due probably to a greater rate of reaction to form alkylate.

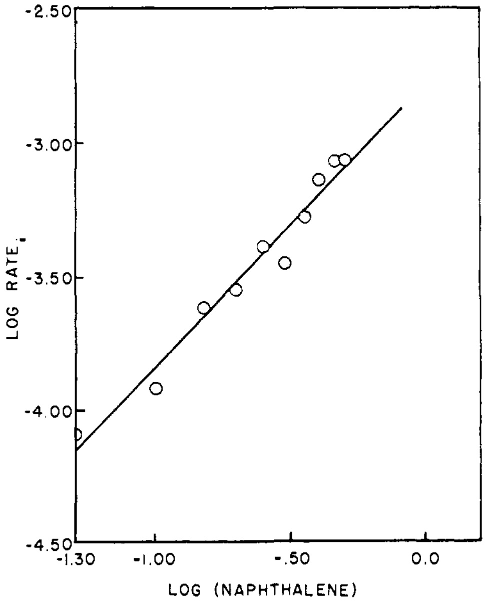

Figure 7. Kinetic order in naphthalene: van't Hoff method; slope = 1.07 ± 0.03 (method of averages); 74.41 ± 0.02°; (RLi) = 0.720 *M;* (ROLi) = 0.235 *M.*

No evidence was found for the existence of an equilibrium between the addition product and alkylate. Reactions of 1- and 2-*t*-butylnaphthalenes with *t*-butyllithium or lithium hydride under alkylation conditions failed to yield intermediate addition product.

**Total Reaction Kinetics.** In attempts to fit the data for the total reaction to various rate equations, it was found that the best fits were obtained with pseudo-first-order plots (Figure 6). Table II records several total kinetic reactions, the ultimate yield of aromatic compounds based on *t*-butyllithium (the yield-limiting reactant), and the per cent of the reaction for which a first-order plot appears linear.

**Table II.** Extent of Pseudo-First-Order Appearance of the Addition–Alkylation Reaction

| Reaction temp, °C | % yield of RLi-derived compd | % total reacn fitting first-order kinetics |
|---|---|---|
| 101 ± 1 | 68.4 | 86.8 |
| 100.0 ± 0.5 | 62.4 | 87.7 |
| 101.0 ± 0.5 | 65.7 | 76.8 |
| 73.5 ± 0.5 | 96.3 | 84.3 |

Although association of addition product and unreacted *t*-butyllithium could lead to experimentally false kinetic relationships, it was considered that the observance of first-order kinetics in such a case would be extremely coincidental. Furthermore, studies of addition product precipitated from the reaction mixture failed to indicate the presence of significant amounts of *t*-butyllithium.

The over-all first-order kinetics might be explained by either: (1) involving only one of the reactants in the rate-determining step; or (2) invoking the reaction of a previously formed complex in the rate-determining step. To choose between these possibilities the kinetic order in each of the reactants was determined by the van't Hoff method.[8]

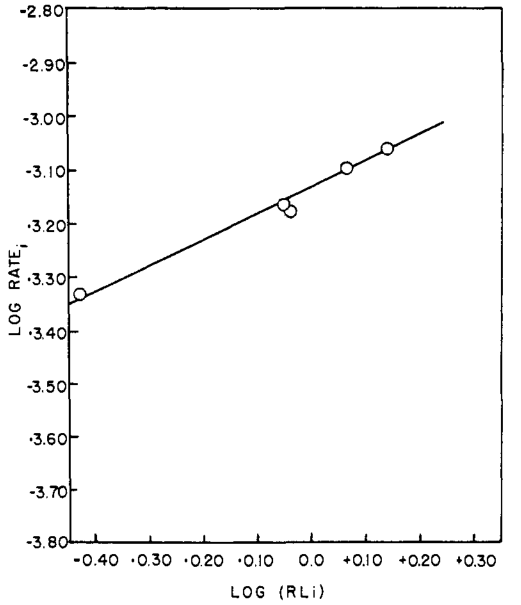

Figure 8. Kinetic order in *t*-butyllithium: van't Hoff method; slope = 0.46 ± 0.03 (method of averages); 74.45 ± 0.02°; (naphthalene) = 0.378 *M*; (ROLi) = 0.430 *M*.

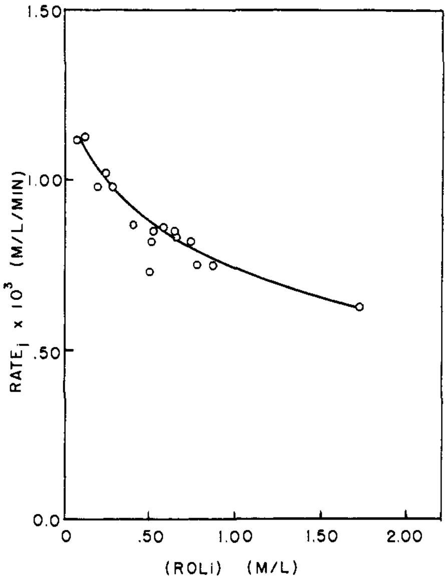

Figure 9. The effect of lithium *t*-butoxide upon the addition of alkylation reaction: 74.35 ± 0.02°; (naphthalene) = 0.450 *M*; (RLi) = 0.820 *M*.

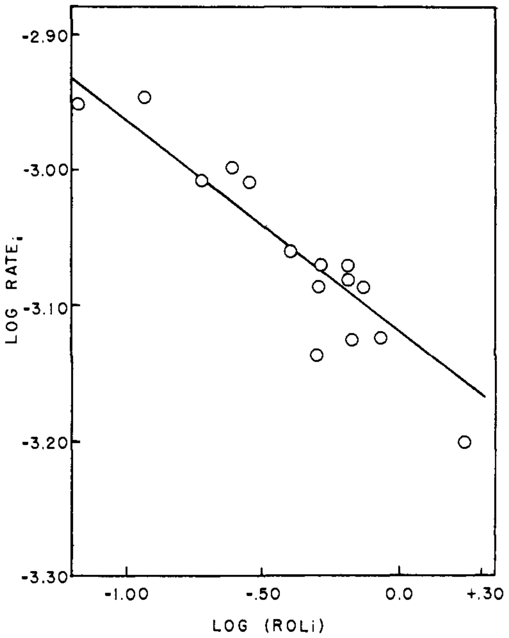

Figure 10. The apparent kinetic order in lithium *t*-butoxide: van't Hoff method; slope = −0.20 ± 0.05 (method of averages); log–log plot of data from Figure 9.

## Kinetic Orders in the Reactants

**Naphthalene.** Duplicate determinations of the order in naphthalene resulted in the values of 1.13 ± 0.08 and 1.07 ± 0.03. Figure 7 shows the van't Hoff plot for the latter determination. A kinetic order of 1 was assigned to naphthalene.

***t*-Butyllithium.** Early measurements of the kinetic order in *t*-butyllithium gave a variety of fractional values. It was found that this nonreproducibility was caused by lithium *t*-butoxide which had a significant effect upon the initial reaction rate. Determination of the order using solutions of differing concentrations of reactants but identical concentrations of alkoxide yielded a reproducible value of 0.46 ± 0.03. Figure 8 shows the data from which this order was calculated. A kinetic order of $^1/_2$ was assigned to *t*-butyllithium. A study by Hartwell and Brown[9] of the intermolecular exchange of RLi between *t*-butyllithium and lithiomethyltrimethylsilane has also indicated a kinetic order of $^1/_2$ in *t*-butyllithium and it has been observed in this laboratory that the thermal decomposition of *t*-butyllithium in hydrocarbon solution exhibits $^1/_2$-order kinetics.[10]

**Lithium *t*-Butoxide.** Except for studies of the thermal decomposition of alkyllithium reagents,[11,12] it is our opinion that investigators of the kinetics of organolithium reactions have not always shown a sufficient concern for the possible effects of alkoxide. Figure 9 shows the effect of added lithium *t*-butoxide upon the initial rate of the addition–alkylation reaction.

Assuming the validity of applying the van't Hoff treatment to the alkoxide, kinetic orders of −0.20 ± 0.05 and −0.24 ± 0.04 were determined. Figure 10 is the plot from which the former value was calculated. Although lack of experimental precision does not permit distinguishing among kinetic orders of $-{}^1/_6$, $-{}^1/_5$, or $-{}^1/_4$, the last value was assigned as the kinetic order in lithium *t*-butoxide.

From the reactant orders determined by the van't Hoff method, the rate equation for initial conditions may be written

$$\text{rate}_i = k\frac{(\text{naphthalene})((t\text{-butyllithium})/4)^{1/2}}{(\text{lithium } t\text{-butoxide})^{1/4}}$$

Division of the monomeric concentration of *t*-butyllithium by 4 corrects for the tetrameric structure of this species in hydrocarbon solution.[13]

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(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 45.

(9) G. E. Hartwell and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4625 (1966).

(10) R. L. Eppley and J. A. Dixon, submitted for publication.

(11) R. A. Finnegan and H. W. Kutta, *J. Org. Chem.*, **30**, 4139 (1965).

(12) W. H. Glaze and G. M. Adams, *J. Am. Chem. Soc.*, **88**, 4653 (1966).

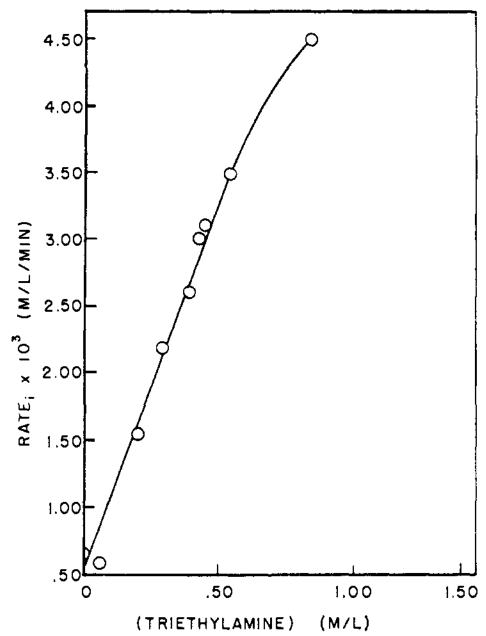

Figure 11. The effect of triethylamine upon the addion–alkylation reaction: 73.40 ± 0.02°; (naphthalene) = 0.502 *M;* (RLi) = 0.449 *M;* (ROLi) = 0.061 *M.*

Since lithium *t*-butoxide concentration remains constant within a reaction, the initial rate equation predicts a total reaction order of 1.5. To test the possibility that experimental errors might not permit distinguishing between a total reaction order of 1 and 1.5, the initial rate equation was rewritten in terms of the reaction variable, *x*, and integrated to yield the equation[14]

$$\text{arc tan}\,[-1.85((\text{RLi})_0 - x)^{1/2}] = k_0t/3.70 + C$$

Using kinetic data which had previously demonstrated a first-order appearance (Figure 6, linear to 84.3% of total reaction), a plot of the arc tangent function was constructed. This plot deviated markedly from linearity, indicating that the total reaction order was indeed 1.

The most direct explanation of the kinetic data appears to be the following: a complex of the form $[(\text{RLi})_2(\text{ArH})]$ is generated rapidly and quantitatively by the reaction of naphthalene with tetrameric *t*-butyllithium. Subsequent reaction of this complex to form addition product in the rate-determining step displays first-order kinetics. For this reason (complex formation), any kinetic study of the total reaction would reveal only a first-order dependence. Rapid complex formation is also supported by $^7$Li nmr, ultraviolet, and cryoscopic studies[15] and by the observation that naphthalene significantly inhibits the initial rate of thermal decomposition of *t*-butyllithium in hydrocarbon solution.[10]

The appearance of lithium *t*-butoxide in the denominator of the initial rate equation suggests that this species forms a complex with *t*-butyllithium in a pre-rate equilibrium reaction[16] and thus limits the amount available for reaction with naphthalene. The value of the order in lithium *t*-butoxide probably reflects the aggregated nature of this compound in hydrocarbon solution.[17] It has been reported that tetrameric *sec*-butyllithium reacts with lithium *sec*-butoxide to form the complex $[(\text{RLi})_2(\text{ROLi})]$.[12]

## Catalysis

Studies in this laboratory of similar reactions employing *n*-butyllithium had indicated that the presence of triethylamine increased the yields of alkylated naphthalenes.[18] When initial reaction rates of *t*-butyllithium with naphthalene were determined as a function of added triethylamines, the plot shown in Figure 11 was obtained. Excluding a mechanism change, the linearity of the plot to a ratio of amine to RLi of *ca.* 1.5 indicates first-order catalysis.

Other investigators[19] have failed to detect any interaction between triethylamine and tetrameric *t*-butyllithium and in this laboratory it has been observed that the amine has no measurable effect upon the initial rate of thermal decomposition of *t*-butyllithium.[10] It has been proposed[19b,c] that the lithium atoms in tetrameric *t*-butyllithium are effectively shielded from triethylamine by the bulky alkyl groups. If this is correct, it may be conjectured that in the alkylation reaction the steric shielding of the lithium atoms is decreased significantly in the rapidly formed complex $[(\text{RLi})_2(\text{ArH})]$. This permits coordination of the amine, resulting in increased nucleophilic character of the carbanion.[20]

This further makes understandable the difference in the influence of the two Lewis bases, lithium *t*-butoxide and triethylamine, on the rate of the reaction. Lithium *t*-butoxide complexes with the *t*-butyllithium tetramer directly, probably by replacing one or more *t*-butyllithium molecules,[21] and thus produces a species which does not form the naphthalene complex required for the addition reaction. In contrast, the triethylamine can only complex with previously formed $(\text{RLi})_2$-ArH species and reaction, rather than being prevented, is accelerated.

When the less basic N,N-dimethylaniline was added to the reaction system no measurable catalysis was observed.

## Activation Parameters

Initial rates for the addition–alkylation reaction were determined at four temperatures and rate constants calculated from the equation

$$k_{\text{exptl}} = \frac{\text{rate}_i(\text{ROLi})^{1/4}}{(\text{ArH})((\text{RLi})/4)^{1/2}}$$

The slope of the Arrhenius plot (Figure 12) and standard equations[22] were used to calculate the parameters listed in Table III. The low entropy of activation is consistent with the reaction of a single, complex species within the rate step.

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(13) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, 1, 654 (1962).

(14) The rate equation was written as: rate = $k(a + bx)(a' + b'x)^{1/2}$ where $a$ = (naphthalene), $a'$ (*t*-butyllithium), $b = -1$, $b' = -1$. Integration was accomplished by the second integral of this form found in "Handbook of Chemistry and Physics," C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1959, p 251.

(15) I. L. Adler, R. L. Eppley, and J. A. Dixon, to be published.

(16) E. Berliner, *J. Am. Chem. Soc.*, 72, 4003 (1950).

(17) G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, 3, 1656 (1964).

(18) J. A. Dixon and R. S. Dudinyak, unpublished.

(19) (a) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, 86, 2135 (1964); (b) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, 86, 2076 (1964); (c) C. G. Screttas and J. F. Eastham, *ibid.*, 87, 3276 (1965).

(20) Activation of an incipient carbanion by a nucleophilic coordination has been suggested by R. E. Dessy and W. Kitching, *Adan. Organometal. Chem.*, 4, 280 (1966).

(21) T. L. Brown, T. A. Ladd, and G. N. Newman, *J. Organometal. Chem.* (Amsterdam), 3, 1 (1965).

(22) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 98–100.

Table III. Activation Parameters for the Addition–Alkylation Reaction[a]

$E_a$ = 25.7 kcal/mol
$A$ = 6.2 × $10^{11}$ l.$^{1/4}$/mol$^{1/4}$ sec
$\Delta H^*$ = 25.0 kcal/mol
$\Delta G^*$ = 25.5 kcal/mol
$\Delta S^*$ = −1.15 eu

[a] $k_{\text{exptl}}$ = 2.81 × $10^{-3}$ l.$^{1/4}$/mol$^{1/4}$ min at 74.58°.

## Miscellaneous Experiments

The following relative reactivities were obtained from initial rate studies: naphthalene = 115 × benzene; 2-*t*-butylnaphthalene = 72 × 1-*t*-butylnaphthalene. The relative reactivity of naphthalene to benzene found here is significantly larger than the value of 30 listed by Williams[23] for free-radical alkylations of these same materials.

Since it was of interest to investigate the possibilities of radical formation within the naphthalene–*t*-butyllithium reaction system an addition–alkylation reaction was monitored by esr. The ability of naphthalene to form a radical anion which displays a diagnostic esr signal is well known.[24] Only a very weak singlet was detected throughout the reaction and this singlet was identical with that recorded for the decalin solution of *t*-butyllithium employed for the reaction.

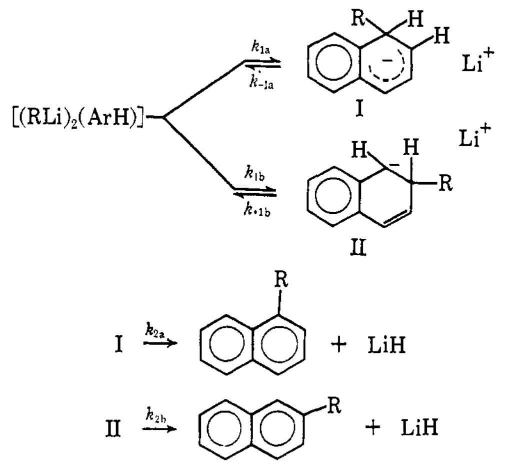
## Summary

The kinetic data indicate the quantitative formation of a complex of the form [(RLi)$_2$(ArH)] in a rapidly established pre-rate equilibrium reaction. The following and rate-determining step appears to be addition of RLi to ArH within the confines of this complex. The following scheme summarizes the proposed mechanism.

$$\tfrac{1}{2}(\text{RLi})_4 + \tfrac{1}{4}(\text{ROLi})_4 \overset{K_1}{\rightleftharpoons} [(\text{RLi})_2(\text{ROLi})]$$

$$\tfrac{1}{2}(\text{RLi})_4 + \text{ArH} \overset{K_2}{\rightleftharpoons} [(\text{RLi})_2(\text{ArH})]$$

RLi = *t*-butyllithium
ROLi = lithium *t*-butoxide
ArH = naphthalene



Since the ultimate alkylation product is composed of *ca.* 70% 1-*t*-butylnaphthalene, and since the addition product I leading to this material is more thermodynamically stable than isomer II (by anion delocalization), $k_{1a}$ is believed larger than $k_{1b}$. This is consistent with the Hammond postulate for endothermic reactions.

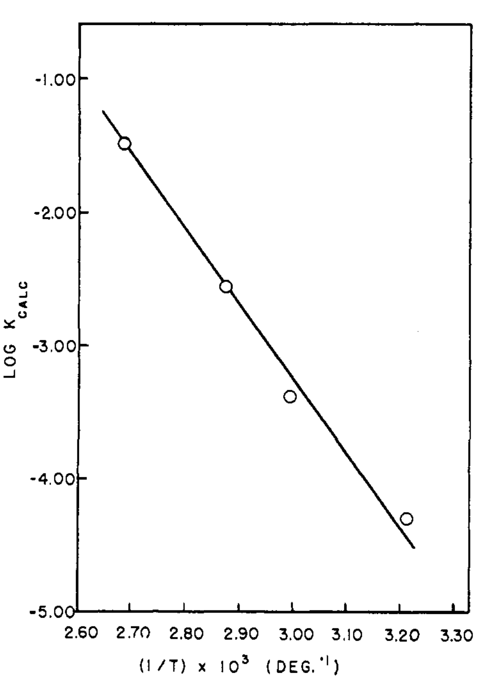


Figure 12. Arrhenius plot for the addition–alkylation reaction: $k_{\text{calcd}}$ = rate$_i$(ROLi)$^{1/4}$/(ArH)(RLi/4)$^{1/2}$; (ROLi)$_0$ = 0.082 *M*.

The constants $k_{1a}$ and $k_{1b}$ must also be larger than $k_{2a}$ and $k_{2b}$, respectively, to account for the concentration profiles observed for the intermediate addition product. Similarly, the greater initial rate of formation of 2-*t*-butylnaphthalene compared to 1-*t*-butylnaphthalene requires that $k_{2b} > k_{2a}$.

## Experimental Section

**Reagents.** All hydrocarbon solvents were rendered unsaturate free by reacting with concentrated sulfuric acid, washing with water, and passing the organic material through a column containing activated alumina. The solvents were dried over Linde Molecular Sieve 4A or calcium hydride. Vpc analysis of this material indicated a minimum purity of 99%. Removal of dissolved reactive gases was accomplished either by a freeze–thaw–evacuation technique or by bubbling purified nitrogen through the liquid stored over Linde Molecular Sieve 4A.

Standard decalin (Matheson Coleman and Bell) solutions of naphthalene (Fisher Scientific, sublimed) were prepared by weight. Purity of the naphthalene was confirmed by a molecular weight determination in freezing cyclohexane (found, 128.10 g/mol; theory 128.12 g/mol).

Decalin solutions of *t*-butyllithium were prepared by evaporating the pentane from a commercial solution (Alpha Inorganics) and replacing it with decalin. Analyses of these solutions for total kinetic reactions were performed by measurement of the volume of isobutane evolved upon quenching an aliquot in a saturated aqueous solution of sodium chloride. A modified Zerewitinoff apparatus was used as the measuring device. This procedure has been discussed by Finnegan.[11] For all other reactions of *t*-butyllithium, analyses were performed by the triphenylmethane method reported previously by this laboratory.[25]

Lithium *t*-butoxide (Lithium Corporation of America) was used without further treatment. The equivalent weight of this material as determined by titration was found to be 80.2 g/equiv (theory, 80.1 g/equiv).

Triethylamine (Eastman White Label) was distilled from calcium hydride and stored over Linde Molecular Sieve 4A. N,N-Dimethylaniline was similarly treated.

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[23] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960.

[24] D. E. Paul, D. Tipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

[25] R. L. Eppley and J. A. Dixon, *J. Organometal. Chem.* (Amsterdam), **8**, 176 (1967).

**Kinetics.** The total addition–alkylation reactions were performed in a vessel constructed to permit separate preheating of the RLi and ArH solutions. The vessel was attached to a vacuum line and was evacuated, flamed, and nitrogen flushed three times prior to charging the reactants. Heating was accomplished within a constant temperature bath capable of maintaining ±0.02°. Stirring was achieved magnetically. Reaction samples were obtained with a hypodermic syringe inserted through a septum-sealed side arm. Samples were immediately quenched by injection into a large excess of water or methyl iodide. After separation and drying, the organic layer was analyzed by vpc.

Vpc analyses were conducted using an 8 ft × 0.25 in. copper column packed with 20% CDS (cyclohexanedimethanol succinate; Applied Science Laboratories) on Chromosorb P 30–60. Instrumental conditions were: column temperature 208°; helium carrier gas flow rate 80 cc/min, uncorrected. Prior to adoption of kinetic analysis by this method, an intensive vpc investigation was conducted to ensure measurement of all significant aromatic components. Although a dialkylated naphthalene was detected in reactions at 100° and above, the concentration never exceeded *ca.* 2% of the total aromatic content when naphthalene was charged in excess.

For the water-quenched kinetic samples, four peaks were observed (omitting solvent). These components had previously been isolated and identified[2] as: naphthalene, hydrolyzed addition products, 2-*t*-butylnaphthalene, and 1-*t*-butylnaphthalene. For the methyl iodide quenched samples four additional peaks were observed. One peak corresponded in retention time to an authentic sample of 1-methylnaphthalene. The three remaining peaks were assumed to be the possible methylated addition products (the total weight percentage of these three agreed with that predicted by analysis of a duplicate sample quenched with water). No peaks corresponding to 2-methylnaphthalene or to 1- or 2-iodonaphthalene were detected.

For the kinetic analyses by vpc, the weight percentages of the aromatic components were calculated from the measured areas (Disc Integrator) and converted to moles/liter by assuming a constant total aromatic concentration equal to the initial naphthalene concentration. Multiplicative area corrective factors determined from known mixtures were employed to compensate for detector response and thermal conductivity effects.[26]

Reactions from which initial rates were calculated were quenched after times estimated to yield *ca.* 10% reaction. These samples were analyzed by the aforementioned vpc procedure. The initial rate reactions were performed in septum-sealed test tubes, which were evacuated, flamed, and nitrogen flushed three times prior to charging. All transfers of materials were made with Hamilton gas-tight syringes.

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# Reactions of Tetranitromethane. I. Kinetics and Mechanism of Nitration of Phenols by Tetranitromethane

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**Abstract:** The reaction of tetranitromethane with phenol, *p*-cresol, *p*-chlorophenol, *p*-cyanophenol, 4-hydroxyacetophenone, and 2,4,6-trimethylphenol (30°, solvent $H_2O$, $\mu = 0.1$) has been found to follow the rate expression $v = k_r$[phenoxide ion][tetranitromethane] over extended ranges of pH and total phenol concentration ($\rho = -4.25$). All products of the reaction arise from reactions of a single intermediate, the formation of which is rate determining. These products are trinitromethane anion (*ca.* 100% yield), nitrite ion, nitrophenols, and phenol coupling products (*e.g.*, Pummerer's ketone) which can arise only *via* phenoxide free-radical intermediates. For phenol and the *para*-substituted phenols we find nitrophenols to be the minor component of the products with the major portion of the nitro groups appearing as nitrate ion. For the reaction of 2,4,6-trimethylphenol with tetranitromethane, trinitromethane and nitrite ion are quantitatively produced. In 95% ethanol as solvent the reaction has been found to be first order in tetranitromethane and second order in the phenol (determined at one acidity) for 2,4,6-tri-*t*-butylphenol and 2,4,6-trimethylphenol, but first order in tetranitromethane and the phenol when phenol and *p*-cresol are employed. Reaction of 2,4,6-tri-*t*-butylphenol with tetranitromethane produces first the visibly identifiable 2,4,6-tri-*t*-butylphenoxide radical which then yields the coupling product 4-nitro-2,4,6-tri-*t*-butylcyclohexa-2,5-dien-1-one. We propose, as the simplest mechanism to explain these results, initial charge transfer complex formation between tetranitromethane and phenoxide ion (in water a 1:1 complex and in ethanol for cases that are second order in phenol and first order in tetranitromethane a 2:1 complex) followed by the rate-determining step of electron transfer and production of $[\mathrm{XPhO}\cdot + \mathrm{NO_2}\cdot + (\mathrm{NO_2})_3\mathrm{C}^-]$. In steps which are not rate controlling nitrophenol arises from coupling of $\mathrm{NO_2}\cdot + \mathrm{XPhO}\cdot$, phenol condensation products from coupling of $\mathrm{XPhO}\cdot$ species, and nitrite ion by reaction of $\mathrm{NO_2}\cdot$ with additional $\mathrm{XPhO}^-$ and anionic phenol coupling products (see Scheme I).

Tetranitromethane was investigated as a nitrating agent for reactive aromatic compounds by Schmidt and Fischer in 1920.[3] It was reported that high yields of mononitrated aniline derivatives were obtained from reactions with aniline carried out in pyridine–ethanol solution. The reaction of *p*-cresol under similar conditions was reported to provide a 60% yield of 4-methyl-2-nitrophenol. However, attempts to nitrate anethole with the reagent under more drastic conditions led to

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