

## KINETICS OF THE CLEAVAGE OF TETRAHYDROFURAN BY n-BUTYLLITHIUM IN HYDROCARBON SOLVENT

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### SUMMARY

The kinetics of the cleavage of tetrahydrofuran by n-butyllithium were studied in hexane solvent. It was found that the order with respect to n-butyllithium was 1 while the order with respect to tetrahydrofuran was 2.5. The frequency factor was found to be  $3.14 \times 10^{15}$  and the Arrhenius activation energy was 27.1 kcal/mole.

### INTRODUCTION

The cleavage of tetrahydrofuran by n-butyllithium is well known; however, the kinetics of the reaction have not been extensively studied. Potter<sup>1</sup> determined a rate constant for the reaction at 35° using an NMR technique. Gilman<sup>2</sup> studied the stability of n-butyllithium in tetrahydrofuran but did not report any rate data.

It has been reported<sup>3</sup> that a catalyst system composed of mixtures of n-butyllithium and tetrahydrofuran can initiate anionic polymerization reactions, and the use of tetrahydrofuran as a solvent for alkylolithiums in metalation reactions<sup>4</sup> is well known. Because of the large number of possible applications for n-butyllithium solutions in tetrahydrofuran an investigation was carried out to determine some basic kinetic parameters for the cleavage of tetrahydrofuran. In this investigation hexane was used as a diluent, and the n-butyllithium concentration was about 0.2 molar in each experiment. The tetrahydrofuran concentration was much larger than the n-butyllithium concentration in each case, thus a pseudo order was determined with respect to n-butyllithium.

### EXPERIMENTAL

The rate experiments were carried out in a one-liter, three-necked flask equipped with a stirrer. Known volumes of the solvent, hexane, and the reactant, tetrahydrofuran, were distilled directly into the reactor under a blanket of nitrogen. The reaction was started by injecting n-butyllithium into the reactor with a syringe through a rubber septum. Samples for analysis were withdrawn with a syringe through the rubber septum. The reactor was immersed in a constant temperature

mineral oil bath. It was found that the temperature could be held constant within  $\pm 0.05^\circ$ .

### *Analysis*

The rate studies were carried out by periodically removing two aliquots from the reaction mixture and determining the n-butyllithium content. The method of analysis was a modified Gilman<sup>5</sup> double titration. To one aliquot was added an excess of 1,2-dibromoethane which reacts with n-butyllithium but not with any ROLi or lithium oxide under the analytical conditions. Both aliquots were then hydrolyzed and titrated with acid. The difference in the two titration values indicated the quantity of n-butyllithium which was present.

### *n-Butyllithium*

The n-butyllithium used in the experiments was a concentrated product (94%) commercially available from the Lithium Corporation of America.

### *Tetrahydrofuran*

The tetrahydrofuran used in the experiments was Fisher "Certified" reagent. It was purified according to the method of Fieser<sup>6</sup> and stored over lithium aluminum hydride. Immediately before an experiment the tetrahydrofuran was distilled directly into the reactor.

### *Hexane*

Matheson Coleman and Bell reagent grade hexane was used in the experiments. The hexane was distilled from finely divided sodium hydride directly into the reactor immediately before each experiment.

### *Reaction products*

The products of the reaction between n-butyllithium and tetrahydrofuran have been reported elsewhere<sup>1</sup> to be butane, ethylene and the lithium enolate of acetaldehyde which, upon hydrolysis, is converted to acetaldehyde. The reaction products from these kinetic experiments were not exhaustively characterized since they had already been adequately described; however, the solid precipitate remaining at the end of an experiment was hydrolyzed and the hydrolysis product was identified as acetaldehyde by the semicarbazone derivative. This product is consistent with Potter's<sup>1</sup> results.

## RESULTS

### *Order with respect to n-butyllithium*

The runs were all made with a large excess of tetrahydrofuran in order to determine an order with respect to n-butyllithium. It was found that the reactions were all pseudo-first-order as evidenced by the fact that plots of the logarithm of the n-butyllithium concentration as a function of time were linear. A similar pseudo-first-order reaction was reported by Potter<sup>1</sup>.

The kinetic expression for the pseudo-first-order reaction can be written as:

$$\frac{d[\text{n-BuLi}]}{dt} = K \cdot [\text{n-BuLi}] \quad (1)$$

where  $K$  is the pseudo-first-order rate constant.

*Order with respect to tetrahydrofuran*

The pseudo-first-order rate constant from eqn. (1) can be written as

$$K = k \cdot [\text{THF}]^n \quad (2)$$

where  $k$  is the rate constant and  $n$  is the order with respect to tetrahydrofuran. Eqn. (2) can be written as:

$$\log K = \log k + n \log [\text{THF}] \quad (3)$$

This equation provides a means of evaluating the order,  $n$ . The logarithm of the pseudo-first-order rate constant is plotted as a function of the logarithm of the tetrahydrofuran concentration and the slope of the plot is equal to the order with respect to tetrahydrofuran.

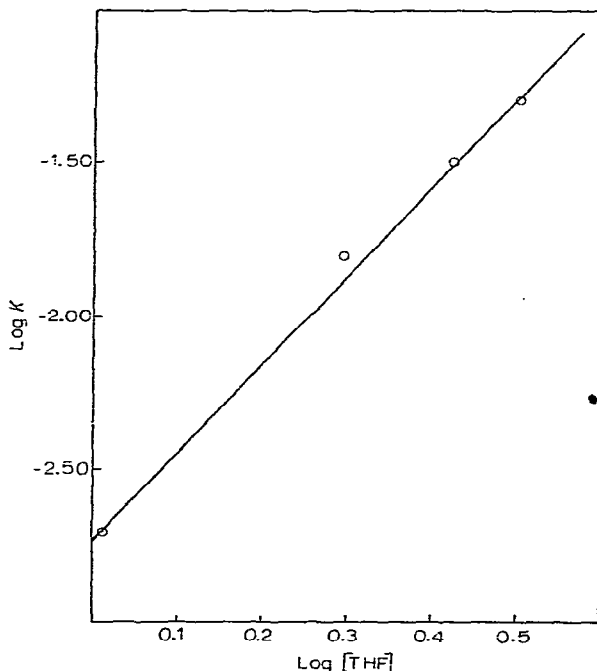


Fig. 1. Logarithm of the pseudo-first-order rate constant as a function of the logarithm of the tetrahydrofuran concentration. Temperature  $-53.7^\circ$ .

A plot of the logarithm of the pseudo-first-order rate constant, observed at  $53.7^\circ$ , as a function of the tetrahydrofuran concentration is shown in Fig. 1. It can be seen that the plot is linear and the slope, determined by statistical methods, is 2.5. The rate equation can now be written as:

$$\frac{d[\text{n-BuLi}]}{dt} = k \cdot [\text{n-BuLi}] \cdot [\text{THF}]^{2.5} \quad (4)$$

*Reaction rate constants*

The reaction rate constants were determined from the pseudo-first-order rate constants by substituting in eqn. (2). Reaction rate constants and reaction parameters are shown in Table 1. The pseudo-first-order rate constants are similar in magnitude to the one reported by Potter<sup>1</sup> at 35°, where a fifteen-fold excess of tetrahydrofuran was used.

TABLE 1

EXPERIMENTAL PARAMETERS AS A FUNCTION OF THE RATE CONSTANTS

Temp. (°C)	[THF]	[BuLi]	<i>K</i> (min <sup>-1</sup> ) × 10 <sup>2</sup>	<i>k</i> (l <sup>2.5</sup> · mole <sup>-2.5</sup> · min <sup>-1</sup> ) × 10 <sup>3</sup>
34.2	1.49	0.229	0.152	0.569
46.2	2.33	0.220	0.838	1.01
53.7	1.02	0.219	0.299	2.82
53.7	2.48	0.258	2.57	2.66
53.7	1.99	0.132	1.54	2.75
53.7	3.19	0.218	5.30	2.91

*Activation energy and frequency factor*

The Arrhenius activation energy was determined in the usual way from the reaction rate constants measured at three different temperatures and found to be 27.1 kcal/mole. The frequency factor determined from the same set of data was found to be  $3.14 \times 10^{15}$ . The reaction rate constant can now be written as:

$$k = 3.14 \times 10^{15} \cdot e^{-27100/RT} \quad (5)$$

## DISCUSSION

The cleavage mechanism has been discussed by other investigators<sup>1,7,8</sup>. All the proposed mechanisms involve the abstraction of an  $\alpha$ -proton followed by a shift of electrons until ethylene and lithium acetaldehyde enolate are eliminated. Potter<sup>1</sup> presented evidence that the slow step was the metalation of tetrahydrofuran at the  $\alpha$ -position. Neither of the suggested mechanisms leads to the rate expression obtained from this investigation.

The fact that the rate equation is complex and does not correspond to the stoichiometry is an indication that the mechanism is complex. The mechanisms mentioned above should lead to a rate equation which is first order with respect to both butyllithium and tetrahydrofuran. The rate equation derived from the present investigation reveals the expected order with respect to butyllithium but the order with respect to tetrahydrofuran is 2.5 instead of 1. The observed high frequency factor suggests that the transition state is a rather loose complex.

A free radical mechanism might be indicated by the kinetic parameters; however, such a mechanism is rendered less likely on the basis that no radicals could be detected when the reaction was followed by ESR<sup>1</sup>.

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