

**EFFECT OF LITHIUM ALKOXIDES ON THE RATE OF THE REACTION BETWEEN BUTYLLITHIUM AND 1,1-DIPHENYLETHYLENE**

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The influence of some lithium alkoxides on the rate of addition of butyllithium to 1,1-diphenylethylene was examined spectrophotometrically. The alkoxides studied changed the reaction rates by a factor of 0.8 to 4.7 in dependence on the composition of the reaction mixture.

To study the mechanism of addition of organic lithium compounds to the double bond between carbon atoms, the system butyllithium-1,1-diphenylethylene has been used by various authors<sup>1,2</sup>. The effect of lithium alkoxides upon this reaction has not been investigated to date, despite the fact that these alkoxides often appear in the reactions of organic lithium compounds, either as impurities or products of side reactions.

The rate of the reaction between butyllithium and 1,1-diphenylethylene in the presence of various lithium alkoxides was followed spectrophotometrically at the absorption maximum in the region 420–440 nm. In these experiments, a large excess of butyllithium with respect to 1,1-diphenylethylene was used, similarly to the investigations carried out by Evans<sup>1</sup>, so that the rate constant of the reaction could be calculated using the integrated rate equation for a first order reaction,  $k = 1/t \log . [E_{\infty}/(E_{\infty} - E_t)]$ , in which  $t$  is time (h),  $E_{\infty}$  is the final extinction value, and  $E_t$  is extinction at a time  $t$ . The rate constant of the reaction in the presence of an alkoxide was always compared with the constant found for the simultaneous reaction of butyllithium alone under otherwise identical conditions. For the reaction of butyllithium alone, the rate constants were  $0.036 \pm 0.003 \text{ h}^{-1}$  ( $c$  0.1505 mol/l) and  $0.033 \pm 0.003 \text{ h}^{-1}$  ( $c$  0.01505 mol/l). These values are slightly lower than the constants published elsewhere<sup>1</sup>, even if the difference in temperature is taken into account; since, however, they were repeatedly obtained with various samples of butyllithium, and also since it has been the main objective of the present work to compare the effects of alkoxides, this difference has not been studied in more detail. The addition of butyllithium to 1,1-diphenylethylene was investigated in the presence of lithium tert-butoxide, (–)-(1*R*)-menthoxide and butoxide (in equimolar amounts with respect to butyllithium; in the case of tert-butoxide, some other ratios were also used).

These comparisons were made each time for two various concentrations of butyllithium. (Fig. 1, Table I.)

TABLE I

Addition of Butyllithium (*I*) to 1,1-Diphenylethylene (*II*) in the Presence of Lithium Alkoxides (ROLi) in Benzene at 29.1°C

$k_m$  Rate constant for the addition of butyllithium in the presence of ROLi,  $k$  rate constant for the addition of butyllithium without effect of alkoxides.

R	ROLi	<i>I</i>	<i>II</i>	$k_m/k$
	$10^{-2}$ mol/l			
(-)-(1 <i>R</i> )-Menthyl	15.0	15.0	0.101	4.65
(-)-(1 <i>R</i> )-Menthyl	1.50	1.50	0.0101	1.20
tert-Butyl	15.0	15.0	0.101	1.70
tert-Butyl	1.5	1.50	0.0101	0.93
Butyl	12.3 <sup>a</sup>	15.0	0.101	1.43
Butyl	1.1 <sup>a</sup>	1.50	0.0101	0.82

<sup>a</sup> Saturated solution of lithium butoxide in the corresponding solution of butyllithium.

Butyllithium was prepared from dibutylmercury and lithium metal in benzene<sup>3</sup>. Its activity was controlled by titration with a xylene solution of sec-butyl alcohol, with phenanthroline as indicator<sup>4</sup>. In this way, the minimal content of the organo-metallic compound (96%) was determined, related to the total alkalinity of the solutions of butyllithium. Lithium alkoxides, prepared by the reaction of the metal with the corresponding alcohol, were purified by crystallization and were completely free of alcohols<sup>5,6</sup>. All operations involving the organic compounds of lithium were carried out in an argon atmosphere containing 20 p.p.m. oxygen at the utmost. The course of the reactions was followed in quartz flasks with a cell and a three-way cock sealed to them, using Unicam SP 500 spectrometer and a KOL-1 apparatus (Laboratorní přístroje).

It follows from the above results that the effect of the added lithium alkoxide upon the rate of addition of butyllithium to 1,1-diphenylethylene depends, in the first place, on the concentration of the reacting compounds. At a higher concentration of butyllithium ( $c$  0.1505 mol/l; curve 1, Fig. 1) the reaction rate increased after addition of lithium tert-butoxide (in an amount 0.4 to 2 mol of alkoxide per 1 mol of butyllithium); on the other hand, at a lower concentration of butyllithium ( $c$  0.01505 mol/l, curve 2, Fig. 1) the reaction rate remained almost unaffected by li-

thium tert-butoxide. A similar effect could also be observed in the case of lithium butoxide, and even more so with  $(-)$  (1*R*) lithium menthoxide (Table I).

With increasing concentration of lithium tert-butoxide at the same concentration of butyllithium the increase in the reaction rate appears to be steeper within the range 0–1 mol  $(\text{CH}_3)_3\text{COLi/mol C}_4\text{H}_9\text{Li}$  than in the case of an excess of alkoxide within the range 1–2 mol  $(\text{CH}_3)_3\text{COLi/mol C}_4\text{H}_9\text{Li}$  (Fig. 1). As the existence of the equimolar complex  $[\text{C}_4\text{H}_9\text{Li} \cdot (\text{CH}_3)_3\text{COLi}]_x$  has been proved<sup>5</sup>, a possibility arises that this complex may participate in the reaction mechanism of addition, which could be one of the causes of the effect of alkoxide. The fact that lithium tert-butoxide has no effect upon the rate of addition at a lower concentration of butyllithium can be due to the decomposition of the complex alkoxide–organometallic compound in the dilute solution, since its concentration is approximately 50 times lower than that of the solution in which the existence of the complex has been proved.

The different structure of the lithium alkoxide added manifests itself also by a change in the reaction rate. A higher effect upon the changes in the reaction rate was observed with the lithium alkoxides in the following order: butoxide < tert-butoxide <  $(-)$ -(1*R*)-menthoxide (Table I). This kind of effect is apparently determined by a complex of properties of the reacting compounds.

1,1-Diphenylhexyllithium, formed by addition of butyllithium to 1,1-diphenylethylene in the presence of the above lithium alkoxides, always exhibited an absorption maximum shifted by 10–12 nm toward higher wavelengths in comparison

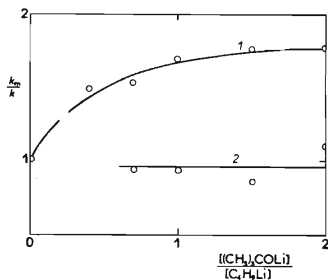


FIG. 1

Change in the Rate of Addition of Butyllithium to 1,1-Diphenylethylene in Dependence on the Concentration of Lithium tert-Butoxide in Benzene at 29.1°C

Symbols for reaction rate constants *cf.* Table I. 1 Butyllithium 0.1505 mol/l, 1,1-diphenylethylene  $1.01 \cdot 10^{-3}$  mol/l; 2 butyllithium 0.01505 mol/l, 1,1-diphenylethylene  $1.01 \cdot 10^{-4}$  mol/l.

with the reaction product of butyllithium itself. A specific solvation of 1,1-diphenylhexyllithium with tetrahydrofuran manifested itself by a similar shift of the absorption maximum<sup>7</sup>, so that an interaction between this organometallic compound and the lithium alkoxides can also be assumed.

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