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NOTE

Kinetics of the thermal decomposition of tert-butyllithium in hydrocarbon solution

In any study of the reactions of alkyllithium reagents at elevated temperatures, one of the possible side reactions to be considered is the elimination of lithium hydride from the alkyllithium to yield an olefin.

Finnegan[1] has reported that the thermal decomposition of n-butyllithium in hydrocarbon solution is a first order reaction and is catalyzed by lithium n-butoxide. Glaze and Adams[2] have found that a one-half order kinetic law describes the decomposition of the tetrameric sec-butyllithium and that alkoxides exert a first order catalytic effect.

During other studies involving tert-butyllithium in this laboratory, we found it desirable to determine the kinetics of the decomposition of this species. Realizing that due to formation of an olefin, the kinetic behavior observed may be to some extent a function of the method of investigation, the decomposition of tert-butyllithium in decalin solution was monitored by three different methods: (*a*) a volumetric procedure utilizing a modified Zerewitinoff[1] apparatus; (*b*) a manometric procedure as employed by Glaze and Adams[2] for sec-butyllithium; and (*c*) a titration procedure, in which reaction aliquots were analyzed for residual tert-butyllithium by the triphenylmethane titration method previously reported by this laboratory[3].

In all cases the rate law which best described the kinetic behavior was $\frac{1}{2}$ order. The effect of alkoxide was not studied but since the concentration of this species remained constant within any single determination, its kinetic effect was also constant.

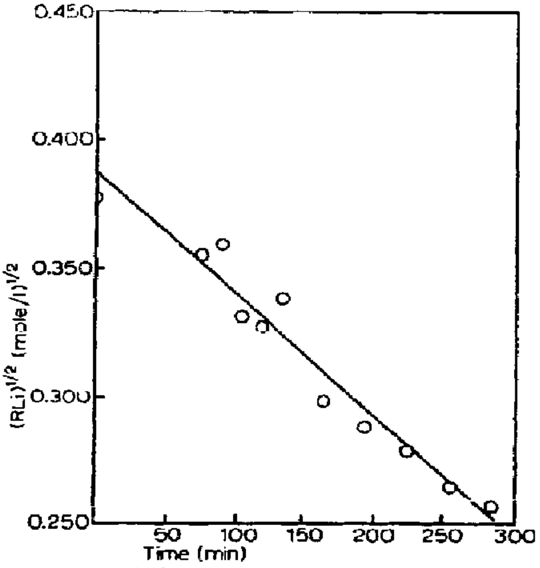

Fig. 1. Kinetic $\frac{1}{2}$ order plot for the thermal decomposition of tert-butyllithium; decalin solvent, triphenylmethane titration procedure, 100°, $[RLi]_0 = 0.143$ mole/l.

Figure 1 shows a typical $\frac{1}{2}$ order plot of the data obtained by the three methods of kinetic analysis. The straight line shown was obtained by applying the Method of Averages to the data.

It was also found that triethylamine had no detectable effect upon the initial rate of decomposition of tert-butyllithium. This is in accord with the reported lack of interaction between these species[4,5]. However, a significant effect by naphthalene was observed. Table 1 and Fig. 2 show the initial rate determined by the volumetric procedure as a function of increasing naphthalene. These data are consistent with the rapid formation of a complex between naphthalene and tert-butyllithium[6,7].

TABLE 1

THERMAL DECOMPOSITION OF TERT-BUTYLLITHIUM

[tert-Butyllithium]$_0$ = 0.786 mole/l; [tert-butoxylithium]$_0$ = 0.020 mole/l.

Run	*Naphthalene (mole/l)*	*Initial rate (ml/min)*
1	0.000	0.25
2	0.089	0.20
3	0.367	0.16
4	0.673	0.08

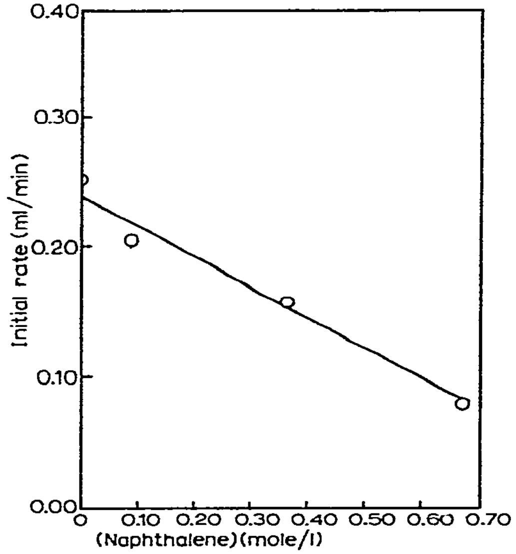

Fig. 2. The effect of naphthalene upon the rate of thermal decomposition of tert-butyllithium; volumetric procedure, decalin solvent, 100°, [RLi]$_0$ = 0.786 mole/l.

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