938. *The Catalytic Action of Anionic Catalyses. Part X.*[1] *The Reaction of Ethyl-lithium with Fluorene and* 1,1-*Diphenylethylene*

By Alwyn G. Evans, C. R. Gore, and N. H. Rees

We previously studied the reaction of n-butyl-lithium with 1,1-diphenylethylene [2] and with fluorene [3] in benzene, and we have now extended these investigations to ethyl-lithium.

Experimental.—The apparatus, preparation of materials, and techniques are the same as used previously.[2,3] Ethyl-lithium was prepared by a method similar to that of Ziegler and Colonius,[4] except that the reactions were carried out in the high-vacuum system. A benzene solution or a pentane solution of ethyl bromide was allowed to react with metallic lithium, filtered, and evaporated to dryness, and benzene was distilled on to the solid ethyl-lithium, the resulting solution being again filtered. Butyl-lithium was prepared as described previously.[2]

Results.—*Orders of reaction.* Experiments in which the ethyl-lithium is in excess show that the reactions are first-order in fluorene and in ethylene (see Figure). The order in ethyl-lithium is low; in its reaction with fluorene it is one-ninth (see Table 1), whilst one-sixth had been obtained for butyl-lithium.[2] This lower order is supported by experiments on the reaction of ethyl-lithium with the olefin, where we find an order of less than one-ninth. (We do not give a specific value in this latter case since the experimental accuracy required to distinguish significantly between orders of one-ninth and less would have to be far greater than is possible at present.)

Temperature-dependence. The temperature-dependence of these reactions and of the reaction of butyl-lithium with fluorene was measured (Table 2). The values of $\Delta H^\ddagger$ are

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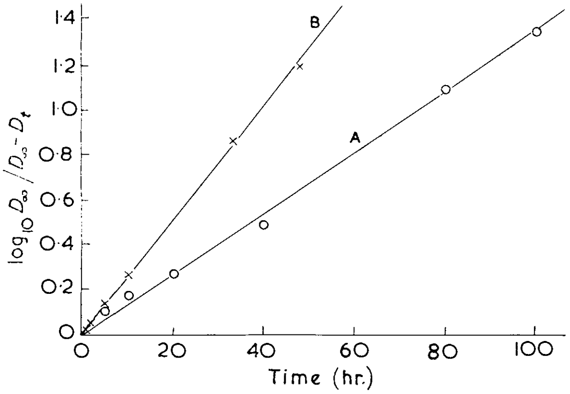
[1] Part IX, A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, 1965, **61**, 1202.

[2] A. G. Evans and D. B. George, *J.*, 1961, 4653.

[3] A. G. Evans and N. H. Rees, *J.*, 1963, 6039.

[4] K. Ziegler and H. Colonius, *Annalen*, 1930, **479**, 135.



Variation of optical density (D) with time, showing the reactions to be first-order in fluorene and in diphenylethylene

Curve A. $[EtLi]_i = 6{\cdot}87 \times 10^{-3}$M. $[Fluorene]_i = 2{\cdot}02 \times 10^{-3}$M. Temp. = 31°c.
D at 345 mμ) = 2·08 (2-mm. cell).
Curve B. $[EtLi]_i = 6{\cdot}48 \times 10^{-4}$M. $[CH_2{:}CPh_2]_i = 1{\cdot}09 \times 10^{-4}$M. Temp. = 30°c.
D at 427 mμ = 2·05 (10-mm. cell).

Table 1

The reaction of fluorene with ethyl-lithium (R_i = initial rate) at 31°

10^3[Fluorene] (M)	$10^3[EtLi]_i$ (M)	R_i (mole l.$^{-1}$ sec.$^{-1}$)	$R_i/([Fl]_i[EtLi]_i^{1/9})$
4·07	60·2	$6{\cdot}33 \times 10^{-8}$	$2{\cdot}1 \times 10^{-5}$
4·08	8·85	$5{\cdot}37 \times 10^{-8}$	$2{\cdot}2 \times 10^{-5}$
4·07	171·0	$7{\cdot}07 \times 10^{-8}$	$2{\cdot}1 \times 10^{-5}$
4·07	6·87	$5{\cdot}26 \times 10^{-8}$	$2{\cdot}3 \times 10^{-5}$
4·07	3·22	$4{\cdot}47 \times 10^{-8}$	$2{\cdot}1 \times 10^{-5}$

Table 2

Temperature-dependence

System	Temp. (°c)	10^6k	
EtLi + Fluorene	19·0	8·76	l.$^{1/9}$ mole$^{-1/9}$ sec.$^{-1}$
	31·6	22·5	,,
	41·4	42·1	,,
	55·0	147	,,
	67·0	327	,,
EtLi + Olefin	20·0	8·8	l.$^{1/9}$ mole$^{-1/9}$ sec.$^{-1}$
	30·3	24	,,
	51·1	170	,,
BuLi + Fluorene	20·8	7·6	l.$^{1/6}$ mole$^{-1/6}$ sec.$^{-1}$
	30·7	16	,,
	40·2	37	,,
	53·3	123	,,
	64·5	234	,,

Table 3

Changes in enthalpy, entropy, and free energy

System	$\Delta H^\ddagger$ (kcal. mole^{-1})	$\Delta S^\ddagger$ (30°) (cal. mole^{-1} deg.$^{-1}$)	$\Delta G^\ddagger$ (30°) (kcal. mole^{-1})
EtLi + $CH_2{:}CPh_2$	17·3	−22·8	24·2
EtLi + Fluorene	14·9	−31·0	24·3
BuLi + $CH_2{:}CPh_2$ (ref. 2)	15·8	−26·4	23·8
BuLi + Fluorene	15·1	−31·0	24·5

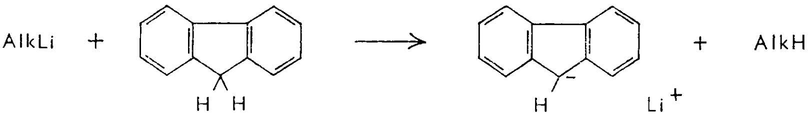
given in Table 3, together with the $\Delta G^\ddagger$ and $\Delta S^\ddagger$ values. (The order in ethyl-lithium in its reaction with the ethylene was taken as one-ninth.)

Discussion.—The results for the ethyl-lithium reactions run parallel to those for butyl-lithium, and may be interpreted, as before, by the equations: [2,3]

$$\frac{1}{x}\{(\mathrm{AlkLi})_x\} \rightleftharpoons \mathrm{AlkLi}$$

$$\mathrm{AlkLi} + \mathrm{CH_2{=}CPh_2} \longrightarrow \mathrm{AlkCH_2{-}\overset{-}{C}Ph_2\overset{+}{Li}}$$

or



in which the associated state of the alkyl-lithium is predominantly the *x*-mer.

The order for ethyl-lithium appears to be less than for butyl-lithium, and we have found this also in recent work using mixed ether–benzene solvents. The degree of association of ethyl-lithium in benzene had been determined earlier, by physical measurements, as 2 [5] and as 6.[6-8]

The activation enthalpies for all these reactions are fairly similar (see Table 3). We should not expect the change from butyl-lithium to ethyl-lithium to make much difference because both involve primary alkyl groups, but it is interesting that the reactions with 1,1-diphenylethylene and with fluorene should give such similar results, since the reactions are of quite different types; the former is the addition of butyl to a double bond, and the latter is a proton abstraction by a butyl group.

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