# The Catalytic Action of Anionic Catalysts. Part XIV.[1] The Reaction of n-Butyl-lithium with Fluorene in Tetrahydrofuran studied by a New Vacuum-type Stopped-flow Apparatus

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We have built a new vacuum-type stopped-flow apparatus to study the reactions of highly reactive anionic species. Reactions having a half-life as low as 5 milliseconds can be followed from room temperature to −80 °C under conditions which rigorously exclude impurities.

Our first measurements by use of this new method have been carried out on the reaction of n-butyl-lithium with fluorene in tetrahydrofuran. The thermodynamic constants of activation determined for this reaction are: $\Delta G^{\ddagger}$ 14·1 kcal mol⁻¹, $\Delta H^{\ddagger}$ 4·7 kcal mol⁻¹, and $\Delta S^{\ddagger}$ −31·2 cal mol⁻¹ K⁻¹.

WE have studied anionic reactions in benzene solution under high-vacuum conditions using normal spectroscopic methods to follow the reaction.[2] When we extended this work to systems in tetrahydrofuran as solvent [1,3] the reaction rate was much too rapid to follow by our earlier technique so we used a vacuum-type stopped-flow method.[4] This method was able to cope with reactions the half-life of which was of the order of *ca.* 5 s, but many of the reactions we wished to study were too fast to be measured in this way, so we have now developed a new stopped-flow apparatus as described in this paper. Our first measurements with this new method have been carried out on the reaction of n-butyl-lithium with fluorene in tetrahydrofuran. The rate of this reaction is not extremely high, but it is just beyond the limit of our previous stopped-flow technique [4] which involved a pen-recorder, the response time of which was too slow for this reaction to be accurately followed.

## EXPERIMENTAL

*Materials.*—n-Butyl-lithium, fluorene, and tetrahydrofuran were purified as described earlier.[2,3] The tetrahydrofuran solutions of butyl-lithium were kept at −80 °C

when not in use, to prevent reaction of butyl-lithium with tetrahydrofuran.[3b]

*Stopped-flow Apparatus.*—Although techniques have been developed in the past for examining fast reactions by stopped-flow methods,[5] they have usually dealt with systems which are not very sensitive to air and which, therefore, can be carried out either under atmospheric conditions or under nitrogen. We wished to be able to store solutions which involved highly reactive anionic species in the apparatus for at least 24 h without appreciable decomposition and this meant that the equipment had to stand high-vacuum conditions.

Dewald and Brooks [6] have recently described a high-vacuum, all-glass, stopped-flow apparatus working from room temperature to −40 °C. We required a sensitive thermostatic device operating down to −100 °C in order (*a*) that the low activation energies of the reactions could be measured, and (*b*) that the rates could be slowed to manageable speeds by working at very low temperature. The use of this low temperature makes it impossible to use silicone grease on taps and syringes immersed in the thermostat fluid, or to use rubber O rings for sealing tubes which pass through the thermostat walls as was done by Dewald and Brooks.[6] We have

[1] Part XIII, J. G. Carpenter, A. G. Evans, and N. H. Rees, *J.C.S. Perkin II*, 1972, 1598.

[2] (*a*) A. G. Evans and D. B. George, *J. Chem. Soc.*, 1961, 4653; 1962, 141; (*b*) A. G. Evans and N. H. Rees, *ibid.*, 1963, 6039; (*c*) A. G. Evans, C. R. Gore, and N. H. Rees, *ibid.*, 1965, 5110; (*d*) R. A. H. Casling, A. G. Evans, and N. H. Rees, *J. Chem. Soc. (B)*, 1966, 519.

[3] (*a*) A. G. Evans, M. Ll. Jones, and N. H. Rees, *J. Chem. Soc. (B)*, 1967, 961; 1969, 894; (*b*) J. G. Carpenter, A. G. Evans, C. R. Gore, and N. H. Rees, *ibid.*, 1969, 908; (*c*) A. G. Evans, M. A. Hamid, and N. H. Rees, *ibid.*, 1971, 1110, 2164.

[4] D. Dadley and A. G. Evans, *J. Chem. Soc. (B)*, 1967, 418.

[5] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell Scientific Publications, London, 1964; Q. H. Gibson, 'Stopped-flow Methods in Enzymology,' vol. XVI, 'Fast Reactions,' ed. K. Kustin, Academic Press, New York, 1969, p. 187.

[6] R. R. Dewald and J. M. Brooks, *Rev. Sci. Instr.*, 1970, **41**, 1612.

overcome these difficulties by arranging for the solutions to be pre-cooled in the thermostat after leaving the syringes and before mixing, so that all the taps and the two syringes are positioned outside the thermostat and all tubes except the collimating tube enter the thermostat from the top so eliminating the necessity of sealing them into the thermostat wall.

In the aqueous systems studied by many previous workers, plastic materials could be used for the mixing device. In our case however, the mixer had to be an all-glass type as has been used by Dewald and Brooks [6] because of the solvents and the reagents involved in these anionic systems.

*Reaction Procedure.*—The stopped-flow apparatus involves a vacuum line with liquid-air trap, diffusion pump, and oil pump, together with a mercury manometer for the regulation of the argon pressure. Solutions of butyl-lithium and fluorene in tetrahydrofuran were made up as described previously [2,3] in flasks fitted with breakseals under high-vacuum conditions. These were attached to the stopped-flow manifold by B19 cones and sockets held together by springs. These cones were fitted with skirts to prevent the solutions from coming into contact with the tap grease (Edwards High Vacuum Silicone Grease), and were arranged so that the solutions could be introduced into the system by rotation of the ampoules about the cones. The whole system was then evacuated and filled at 80 cmHg pressure with argon (Air Products, standard grade) purified by passage through a trap cooled in solid carbon dioxide-methanol. This operation was repeated several times; finally the breakseals were broken in turn and samples of each solution drawn into the appropriate syringe. Sintered glass filters were introduced before the syringes to avoid pieces of broken glass from the breakseals being drawn into the syringe.

All-glass Summit syringes of 5 ml capacity, made by Smith and Nephew, were used. They were carefully chosen for holding vacuum and we found that tetrahydrofuran solutions of triphenylmethylsodium were stable in these syringes for at least ten days when they were sealed just by the solution itself. Solutions from the two syringes were simultaneously ejected pneumatically or by hand (same results obtained in each case) through two coils immersed in the thermostat bath so that the liquids had ample time to reach bath temperature before entering the mixing chamber. These coils also reduced the strain which developed in the glassware when the metal thermostat case was cooled. The design of the tubes connecting the syringes to the mixer was such that if bubbles of argon were trapped in the liquid, they could be removed easily by successive syringing of the solution. Before the mixer, a sintered glass filter was introduced to avoid grease passing into the mixing chamber.

At the observation point, $1\frac{1}{2}$ cm beyond the mixing chamber, the product of the reaction, fluorenyl-lithium, was measured by using monochromatic light of wavelength 481 nm ($\lambda_{max}$ of fluorenyl-lithium [2b]). The reaction curve was obtained by photomultiplier and cathode ray oscilloscope and the trace recorded photographically.

Beyond the observation point and outside the thermostat is a vessel which collects the waste solution (this vessel is essential because we are dealing with a closed system).

Details of various parts of this equipment are given below.

*Thermostat.*—We have designed and tested a new low-temperature thermostat [7] which is proving extremely satisfactory. The temperature can be held to $\pm 0.1$ °C at $-90$ °C. A major difficulty was the sealing of the observation tube into the collimating tube of the optical system in such a way that it could stand very low temperature. We finally used silicone grease to seal the glass into the collimating tube and covered this with aluminium foil to prevent erosion by the thermostat liquid (methanol), and this was successful in preventing methanol from leaking into the collimating tube.

*Mixer.*—Various mixing devices have been made by different investigators,[5] some involving as many as 32 jets, in order to make sure that the mixing is thorough before the liquid passes along the tube to the observation point. We found, however, that a two-port tangential-jet all-glass mixer [8] was quite efficient.* This was tested by using an acid-base system with phenolphthalein as indicator, when it was found that at the observation point ($1\frac{1}{2}$ cm from the mixing chamber) the reaction was complete, thus showing that at this point there was no inhomogeneity in the mixing. The time which elapses between mixing and observation is of the order of milliseconds. The rate of flow of the solution past the observation point is of the order of 10 m s$^{-1}$.

*Method of Detection.*—This involved a power supply (Brandenburg 471R), a Bausch and Lomb grating high-intensity monochromator (350—800 nm) with an EMI 9429B photomultiplier, and a smoothing circuit of range 10 μs to 100 ms, which eliminated the noise completely, giving fine, smooth lines for the reaction curves.

*Recording Device.*—This was a Tektronix-model 564 cathode ray oscilloscope (with differential amplifier 2A63, and time base 2B67) having storage facilities. The traces were recorded on Polaroid or 35 mm cameras.

*Analysis of Oscilloscope Traces.*—Curve analysis was made much simpler by using a log converter to convert transmittance into optical density, so that the voltage–time curve which was photographed was directly related to the corresponding optical density–time curve. The log converter was similar to one described,[9] but modified in such a way as to increase the scale over which the transmittance was converted linearly into optical density. The Polaroid photographs were analysed by travelling microscope; the 35 mm frames were projected on to a screen to give an *ca.* 10-fold magnification (linear) which enabled normal analysis to be carried out.

Reproducibility was extremely good; several reactions were carried out under the same conditions and the reaction curves coincided perfectly.

The quantities of solutions required are very much smaller than in our previous stopped-flow apparatus [4] and this makes for greater rapidity of working.

RESULTS

*Orders of Reaction.*—The orders of reaction were found to be 0.5 for n-butyl-lithium and 1.0 for fluorene (Figure and Tables 1 and 2). A value of 0.5 for the order of n-butyl-lithium has been found previously for its reaction with 1,1-diphenylethylene,[3b] triphenylethylene,[1] and Ph$_3$CH [1] in tetrahydrofuran, and with 1,1-diphenylethylene in 0.4% ethanol–benzene.[3b] A value of 1.0 for the order of fluorene has been obtained for its reaction in benzene with n-butyl-

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* Professor E. F. Caldin has also observed this (personal communication).

[7] A. G. Evans, D. W. Michael, N. H. Rees, and N. A. Walker, *Rev. Sci. Instr.*, 1972, **42**, 1706.

[8] H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.*, 1923, A, **104**, 376.

[9] D. McLean and R. L. Tranter, *J. Phys. (E)*, 1971, **4**, 455.

lithium,[2b] ethyl-lithium,[2c] and t-butyl-lithium,[2d] and for its reaction in tetrahydrofuran with three silyl-lithiums.[3c]
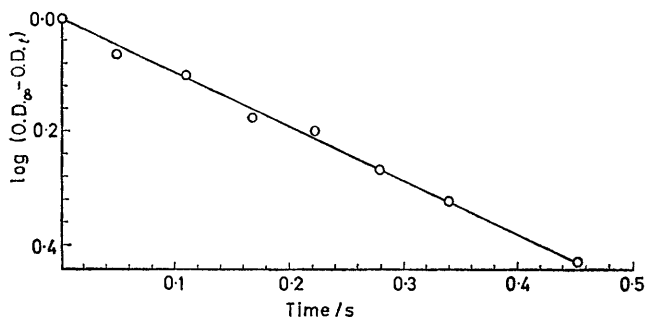


First-order plot of reaction curve at −60 °C. [Fluorene]$_i$ = 8·38 × 10$^{-3}$M. [n-Butyl-lithium]$_i$, expressed as the monomer = 1·81 × 10$^{-1}$M. $k'$ = 2·11 s$^{-1}$

*Temperature-dependence of Reaction Rate.*—The initial rate of reaction was measured over a range of temperatures, and the results are in Table 3. The activation energy so

### TABLE 1

Reaction of n-butyl-lithium with fluorene in tetra-hydrofuran at −60 °C

| 10$^2$[Li$^+$]$_i$/M | 10$^3$[Fluorene]$_i$/M | $k'$/s$^{-1}$ | $\dfrac{k}{\text{l}^{0.5}\ \text{mol}^{-0.5}\ \text{s}^{-1}}$ |
|---|---|---|---|
| 12·37 | 5·87 | 2·70 | 10·9 |
| 7·95 | 8·40 | 2·19 | 11·0 |
| 3·02 | 8·40 | 1·32 | 10·7 |

Rate of reaction = $k'$[Fluorene]

$$= k\left(\frac{[\text{Li}^+]}{2}\right)^{0.5}[\text{Fluorene}]$$

[Li$^+$]$_i$ = total initial concentration of n-butyl-lithium expressed as monomeric butyl-lithium.

[Fluorene]$_i$ = initial concentration of fluorene.

### TABLE 2

| 10$^3$[Fluorene]$_i$/M | 10$^2$[Li$^+$]$_i$/M | 10$R_i$/V s$^{-1}$ | $\dfrac{10^2 R_i/[\text{Fluorene}]_i}{1\ \text{V s}^{-1}\ \text{mol}^{-1}}$ |
|---|---|---|---|
| 25·05 | 9·49 | 130·7 | 5·2 |
| 6·39 | 9·49 | 31·7 | 5·0 |
| 1·72 | 9·49 | 8·8 | 5·1 |

$R_i$ = Initial rate. Initial slope of voltage–time curve is directly proportional to initial slope of optical density–time curve.

obtained was 5·3 kcal mol$^{-1}$. (The small change in extinction coefficient with temperature of fluorenyl-lithium was taken into account in calculating the effect of temperature on the rate of reaction.)

The thermodynamic constants of activation are given in Table 4 for 30 °C. (These results agree well with the preliminary results for this system with our previous stopped-flow method.)

We interpret our results in terms of the reactions (1) and

### TABLE 3

Temperature-dependence of initial rate of reaction

| $T$/K | $R_i$/V s$^{-1}$ | $T$/K | $R_i$/V s$^{-1}$ |
|---|---|---|---|
| 244·0 | 48·20 | 226·0 | 23·83 |
| 243·5 | 57·61 | 226·0 | 23·64 |
| 243·0 | 46·78 | 219·5 | 16·03 |
| 233·0 | 27·83 | 213·0 | 10·91 |

Initial slope of voltage–time curve is directly proportional to initial slope of optical density–time curve.

### TABLE 4

Thermodynamic constants of activation for the reaction of n-butyl-lithium with fluorene in tetrahydrofuran at 30 °C (calculated from experimental results within the −29 to −60 °C region)

| $\dfrac{k}{\text{l}^{0.5}\ \text{mol}^{-0.5}\ \text{s}^{-1}}$ | $\dfrac{\Delta G^{\ddagger}}{\text{kcal mol}^{-1}}$ | $\dfrac{\Delta H^{\ddagger}}{\text{kcal mol}^{-1}}$ | $\dfrac{\Delta S^{\ddagger}}{\text{cal mol}^{-1}\ \text{K}^{-1}}$ |
|---|---|---|---|
| 441 | 14·1 | 4·7 | −31·2 |

Estimated errors: $k$, ±7%; $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, ±5%; $\Delta S^{\ddagger}$, ±10%.

(2) where, if equilibrium (1) lies far to the left, we find equations (3) and (4), and hence (5). These results have

$$\tfrac{1}{2}(\text{BuLi})_2 \underset{b}{\overset{a}{\rightleftarrows}} \text{BuLi} \qquad (1)$$



$$(2)$$
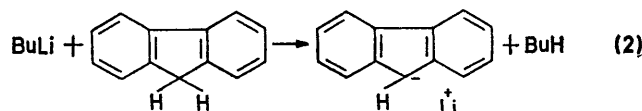
Rate of reaction = $k_2$[BuLi][Fluorene] $\qquad (3)$

$$= k_2\frac{k_{1a}}{k_{1b}}\,[(\text{BuLi})_2]^{0.5}\,[\text{Fluorene}] \qquad (4)$$

$$k = k_2\frac{k_{1a}}{k_{1b}} \qquad (5)$$

been discussed[1] together with the reactions of n-butyl-lithium with fluorene in benzene[2c] and with Ph$_3$CH in tetrahydrofuran and benzene.[1]