Relative Reactivities of Ion-pairs of the 1,3-Diphenylallyl Carbanion towards Fluorene

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The kinetics of the protonation of ion-pairs of the 1,3-diphenylallyl carbanion by fluorene have been studied spectrophotometrically. Where lithium is the counterion, the loose ion-pair reacts about one hundred times faster than the tight ion-pair. The tight ion-pairs of the sodium salts react four or five orders of magnitude faster than the lithium tight ion-pairs.

DIFFERENCES in the reactivities of ion-pairs and free ions have been postulated for some considerable time, but it is only relatively recently that many quantitative measurements have been made. Anionic polymerisation studies have been particularly fruitful and it has been established that usually the propagation rate constant for the free anion is slightly greater than that for the loose ion-pair, and very much greater (often by two or three orders of magnitude) than that for the tight ion-pair. Hitherto, the only exception to this general rule appears to be[1] propylene episulphide whose ion-pair with sodium propagates about three times faster in tetrahydrofuran (THF) than does the free anion. The subject has been reviewed[2] and a compilation of useful data is available.[3]

Studies of proton-transfer reactions involving anions or their ion-pairs are less numerous and the results of these do not exhibit a uniform trend of relative reactivity with the nature of the association. Proton transfer from triphenylmethane to polystyrylsodium[4] gave a much higher rate constant for the free anion than for the ion-pairs; the value of the latter was much greater in dimethoxyethane (DME) than in THF in accordance with the known greater fraction of the more reactive loose ion-pair in DME. The reaction of fluorenylsodium with benzo[*c*]fluorene has an ion-pair rate constant that also was found to be much greater in DME than in THF, again implying that the loose ion-pair is much more reactive than the tight ion-pair.[5] In contrast, the protonation of anthracenepotassium in THF by ethanol was very markedly slowed when the tight ion-pairs were converted into loose ion-pairs by the addition of dicyclohexyl-18-crown-6-ether.[6] Studies of the protonation of anthracenelithium in DME by t-butyl alcohol showed

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[1] P. Hemery, S. Boileau, P. Sigwalt, and B. Kaempf, *J. Polymer Sci., Part B, Polymer Letters*, 1975, **13**, 49.

[2] M. Szwarc, 'Carbanions, Living Polymers and Electron Transfer Processes,' Wiley, New York, 1969.

[3] H. Hirohara and N. Tse, *J. Polymer Sci., Part D*, 1972, 295.

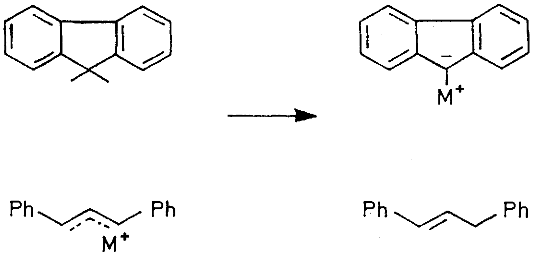
[4] L. L. Chan and J. Smid, *J. Phys. Chem.*, 1972, **76**, 695.

[5] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1967, **89**, 2764.

[6] E. R. Minnich, L. D. Long, J. M. Ceraso, and J. L. Dye, *J. Amer. Chem. Soc.*, 1973, **95**, 1061.

that the free anion is even less reactive than the loose ion-pair.[7] Similarly, the protonation of the benzyl-sodium ion-pair by methanol in THF is 100 times faster than the protonation of the free anion.[8]

The thermodynamics of the ion pairing of the 1,3-diphenylallyl carbanion with the alkali-metal cations has been extensively studied in this laboratory.[9] Preliminary tests showed that these ion-pairs are protonated fluorene.



Scheme 1

This reaction proceeds at a rate which can be monitored spectrophotometrically. The use of fluorene is particularly convenient since the spectra of the ion-pairs of the fluorenyl anion have been well characterised.[10,11]

EXPERIMENTAL

Solvents were purified and dried by distillation from the potassium salt of the di-negative ion of benzophenone. Fluorene was recrystallised from alcohol and dried *in vacuo*. 1,3-Diphenylpropene was prepared and purified as previously described.[12]

The preparation and handling of all solutions was conducted under high vacuum.

Diphenylallyl-lithium in Tetrahydrofuran.—1,3-Diphenylallyl-lithium ($\mathrm{Li^+DPP^-}$) exists in THF virtually exclusively as the loose ion-pair, having an absorption maximum at 564 nm. The extinction coefficient of $\mathrm{Li^+DPP^-}$ was determined by adding a *slight* excess of n-butyl-lithium to a weighted quantity of 1,3-diphenylpropene in a known volume of THF. The progress of the allylic abstraction reaction

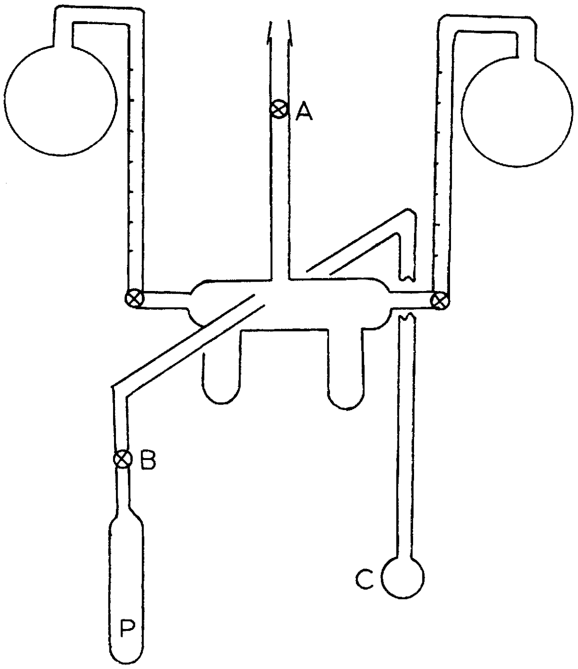
$$\mathrm{PhCH{=}CH{-}CH_2Ph} + \mathrm{C_4H_9Li} \longrightarrow \mathrm{Li^+PhCH{=}CH{-}\bar{C}HPh} + \mathrm{C_4H_{10}}$$

was monitored spectrophotometrically by means of a calibrated quartz cell attached to the reactor, and the limiting absorbance was determined. Duplicate experiments gave the value $\varepsilon = (4.73 \pm 0.12) \times 10^4\ \mathrm{cm^2\ mol^{-1}}$ at 564 nm.

The stock solution of $\mathrm{Li^+DPP^-}$ in THF used for the kinetic studies was prepared by adding n-butyl-lithium to an excess of diphenylpropene, to prevent any possibility of the presence of free butyl-lithium during the subsequent reaction with fluorene. The solution was stored in a flask fitted with a greaseless stopcock.

Butyl-lithium was added to a solution of a weighed quantity of fluorene in a known volume of THF until *ca.* 5% was converted into fluorenyl-lithium ($\mathrm{Li^+Fl^-}$), thus positively ensuring that the solution was free of reactive impurities, such as water. The concentration of $\mathrm{Li^+Fl^-}$ was determined spectrophotometrically using the literature value[10] ($9.60 \times 10^3\ \mathrm{cm^2\ mol^{-1}}$) for the band at 273 nm; the concentration of fluorene was determined by difference. The accuracy of this procedure was confirmed spectrophotometrically by treating an aliquot of this stock solution with sufficient butyl-lithium to ensure complete conversion of the fluorene into $\mathrm{Li^+Fl^-}$.

The reaction vessel (see Figure) consisted of a flask bearing the reservoirs of stock solutions, a purge reservoir P containing $\mathrm{Li^+DPP^-}$, and a quartz cell C of 0.1 cm pathlength. The reactor was flamed under vacuum and when cool, stopcock A was closed and the apparatus removed from the vacuum line. The purge solution of $\mathrm{Li^+DPP^-}$ was introduced into the reactor to destroy any residual moisture or other impurities adsorbed on the walls and was then returned to the reservoir. The reactor was thoroughly rinsed by distilling in solvent from the purge solution. The washings were returned to the reservoir and stopcock B was closed. Known volumes of the stock solution of $\mathrm{Li^+DPP^-}$ and of fluorene were separately introduced into the legs of the reactor by means of the integral burettes. The solutions were mixed and introduced into the cell which was immersed in an unsilvered Dewar vessel filled with alcohol and located in the cell compartment of a Perkin-Elmer 137 spectrophotometer. The latter was fitted with a time-drive motor which enabled the reaction to be monitored at constant wavelength.



One unexpected phenomenon deserves mention. In an early set of experiments occasional anomalously high rates were observed. The cause of this effect proved to be the use of a purge consisting of $\mathrm{Na^+DPP^-}$ in THF. Investigation showed that some insoluble sodium compound was formed in the reactor which subsequently exchanged

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[7] A. Rainis, R. Tung, and M. Szwarc, *Proc. Roy. Soc.*, 1974, *A*, **339**, 417.

[8] B. Bockrath and L. M. Dorfman, *J. Amer. Chem. Soc.*, 1974, **96**, 5708.

[9] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 835.

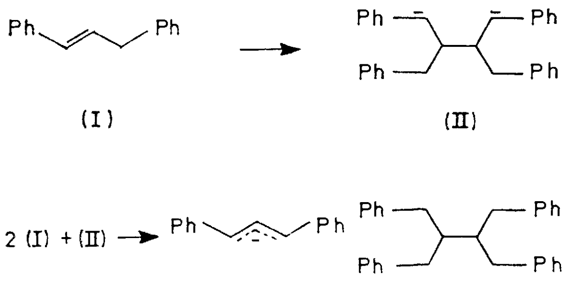
[10] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307.

[11] L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, 1968, **90**, 4654.

[12] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*C*), 1971, 3780.

cations with the stock solution of Li^+DPP^- when the latter was introduced. Accordingly, care was always taken thereafter to ensure that the salt of DPP^- employed in all purges was the same as that in the stock solution.

Diphenylallylsodium in THF.—The stock solution of Na^+DPP^- was prepared by the reduction of 1,3-diphenylpropene in THF by a sodium mirror generated by the thermal decomposition of sodium azide. The solution was filtered through a sintered disc and stored in a reservoir fitted with a greaseless stopcock. The reduction has been shown [13] to take the course shown in Scheme 2. Whilst this was a convenient means of preparing Na^+DPP^- the limiting absorbances were inadequately reproducible for this procedure to serve as a basis for determining the extinction coefficient. The latter was measured indirectly using the apparatus of Figure 1 with one reservoir and the purge vessel containing Na^+DPP^- in THF and the other reservoir containing a solution of fluorene in THF. After purging and rinsing the reactor, a known volume of the solution of Na^+DPP^- was introduced and the absorption spectrum was recorded. The latter consisted of a strong absorption at 524 nm and a weak band at 560 nm respectively corresponding to the tight and loose ion-pairs in the concentration ratio 4 : 1. A small known volume of the fluorene solution was added, the solution was thoroughly mixed, and the spectrum was again recorded. It was found that the bands due to Na^+DPP^- had diminished in intensity whilst those corresponding to the formation of Na^+Fl^- had appeared, comprising a maximum at 358 nm with a shoulder at 372 nm in addition to weaker bands at 436, 459, and 488 nm. This change in the spectrum was effectively instantaneous. By further successive additions of fluorene, this titration was continued to beyond the end-point, the spectrum being recorded after every addition. Using the literature value [10] for the extinction coefficient of Na^+Fl^- in THF (1.08×10^4 cm^2 mol^{-1} at 358 nm) the course of the titration was analysed in detail, yielding the value 5.7×10^4 cm^2 mol^{-1} for the extinction coefficient of Na^+DPP^- in THF at 524 nm. A similar titration using more dilute solutions and a 1.0-cm cell gave the same result.



SCHEME 2

The stock solution of fluorene used for the kinetic studies was prepared by dissolving a weighted quantity of fluorene in a known volume of THF and titrating in sufficient Na^+DPP^- to convert some 5% of the fluorene into Na^+Fl^-. This was conveniently achieved using the apparatus shown in the Figure. The kinetic studies were also conducted using this apparatus, but bearing a 10-cm cell and by monitoring the absorbance at 524 nm.

Diphenylallyl-lithium in 2,5-Dimethyltetrahydrofuran.—Preliminary tests showed that the reaction between Li^+DPP^- and fluorene in 2,5-dimethyltetrahydrofuran (DMTHF, equimolar mixture of *cis*- and *trans*-isomers) was extremely slow. To avoid the risk of the failure of greaseless stopcocks over such a long period, the solutions of Li^+DPP^- and of fluorene (containing 5% of Li^+Fl^-) were prepared in ampoules fitted with break-seals and fused on to an all-glass reactor bearing a quartz cell of 0.1-cm path-length. The extinction coefficient of Li^+Fl^- was determined as 9.3×10^3 cm^2 mol^{-1} at 345 nm. By treating a solution of Li^+DPP^- with less than its stoicheiometric equivalent of fluorene and measuring the consequent change in the spectrum, the extinction coefficient of Li^+DPP^- was found to be 3.52×10^4 cm^2 mol^{-1} at 480 nm.

Diphenylallylsodium in DMTHF.—A solution of Na^+DPP^- was prepared by the reduction of diphenylpropene by sodium in DMTHF. Because of the extreme slowness of the reduction, an all-glass apparatus was used, with the final solution being stored in an ampoule fitted with a break-seal. The spectrum of the solution corresponded to the presence of the tight ion-pair and consisted of a band at 513 nm having shoulders at 500 and 430 nm. The extinction coefficient at 513 nm was assumed to be the same as that of Na^+DPP^- in THF, *viz* 5.7×10^4 cm^2 mol^{-1}. Kinetic studies were conducted in an all-glass reactor fitted with a 10-cm quartz cell.

Diphenylallyl-lithium in a THF–DMTHF Mixture.—An ampoule of Li^+DPP^- was prepared in DMTHF as described above together with an ampoule of a solution of fluorene in a mixture of THF and DMTHF. The ampoules were fused to an all-glass reactor attached to a 0.1-cm cell. The resulting reaction mixture contained 12% by volume of THF. The extinction coefficients used were $\varepsilon = 3.5 \times 10^4$ cm^2 mol^{-1} at 480 nm for Li^+DPP^- and $\varepsilon = 9.6 \times 10^3$ cm^2 mol^{-1} at 345 nm for Li^+Fl^-.

Diphenylallyl-lithium in 2,3-Dihydropyran.—The stock solution of Li^+DPP^- was generated in 2,3-dihydropyran (DHP) from diphenylpropene using somewhat less than the stoicheiometric equivalent of butyl-lithium. The extinction coefficient at the absorption maximum (488 nm) was determined as 2.08×10^4 cm^2 mol^{-1} by measuring the absorbance of a solution of diphenylpropene to which a *slight* excess of butyl-lithium had been added. This abstraction of a proton from diphenylpropene by butyl-lithium was remarkable for its extreme slowness—the rate constant was found to be *ca.* 10^{-2} l mol^{-1} s^{-1} at 23 °C. As a consequence of this observation, the stock solution of Li^+DPP^- was stored for several days before use in the kinetic study so as to ensure that no unchanged butyl-lithium would be present. The preparation of the stock solution of fluorene containing 5% of Li^+Fl^- presented no difficulties since the abstraction of a proton from fluorene by butyl-lithium was fast.

RESULTS AND DISCUSSION

The reaction of Li^+DPP^- in THF with fluorene was relatively slow. Accordingly, in addition to monitoring the absorbance at 564 nm as a function of time, it was possible periodically to scan the entire spectrum. The disappearance of the absorption due to Li^+DPP^- was accompanied by the appearance of the bands of Li^+Fl^- at 436, 457, 487, and 524 nm. Successive spectra passed through an isosbestic point, confirming that the protonation of the diphenylallyl carbanion by fluorene was a clean reaction. The results obtained were plotted using the second-order integrated rate equation. Whilst

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[13] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1006.

some reactions produced linear plots, others exhibited an upward curvature. No systematic trend was observed in the extent of curvature with either the concentration of the reagents nor with the age of the stock solutions. Detailed analysis by Flynn's time-ratio method[14] confirmed that the reactions were indeed best described by second-order kinetics. It was concluded that errors in assessing the exact composition of the reaction mixture were responsible and where curvature was observed, the initial slope was used to evaluate the rate constant. The results of experiments conducted at three temperatures are summarised in Table 1. Analysis of these results gave the Arrhenius parameters $E_A = 56$ kJ mol^{-1} and $A = 5 \times 10^9$ l mol^{-1} s^{-1}.

TABLE 1

Rate constants for the reaction of Li^+DPP^- with fluorene in THF

t/°C	$10^4 \times [Li^+DPP^-]$ / mol l^{-1}	$10^4 \times$ [Fluorene] / mol l^{-1}	Rate constant / l mol^{-1} s^{-1}
23.0	4.69	7.92	0.56
	3.82	8.25	0.69
	2.58	8.71	0.57
	3.04	8.55	0.68
	6.59	7.21	0.63
10.0	3.82	8.25	0.21
	2.86	8.61	0.23
	6.56	7.22	0.27
	4.69	7.93	0.20
1.0	5.06	7.78	0.11
	2.58	8.71	0.08
	4.22	8.10	0.11
	6.34	7.31	0.12

Preliminary experiments showed that the reaction of Na^+DPP^- with fluorene in THF was extremely fast. At first it was feared that some unforeseen residual impurity was causing the protonation of the Na^+DPP^- but the spectrum of the reacted mixture corresponded to the formation of Na^+Fl^- in precisely the expected concentration. The rapidity of the protonation posed severe difficulty in ensuring adequate mixing within the lifetime of the reaction. In the absence of a suitable stopped-flow apparatus a partial solution to the problem was found in using larger volumes of the reagents which mixed with sufficient turbulence in a long (10-cm) path-length cell. The results, shown in Table 2, were obtained by the observation of only a few per cent of the reaction and are consequently not of high precision. In the light of the enormous difference from the rate constants for the protonation of Li^+DPP^- in the same solvent this lack of precision is of little consequence.

TABLE 2

Rate constants for the reaction of Na^+DPP^- with fluorene in DMTHF at 23 °C

$10^4 \times [Na^+DPP^-]$ / mol l^{-1}	$10^4 \times$ [Fluorene] / mol l^{-1}	Rate constant / l mol^{-1} s^{-1}
1.04	1.54	2 050
1.10	1.46	800
1.10	1.46	2 000

The reaction of Li^+DPP^- in DMTHF with fluorene was an exceedingly slow reaction in comparison with those hitherto described. The absorption spectrum of Li^+DPP^- consisted of a band at 480 nm with a shoulder at 398 nm. As the reaction proceeded, the intensities of these decreased and a new band appeared at 345 nm corresponding to the formation of the tight ion-pair of Li^+Fl^-. Simultaneously, the intensities of the bands of fluorene at 301, 290, and particularly that at 294 nm appeared to increase, as a result of overlap with the stronger bands of the forming Li^+Fl^-. The extinction coefficient of Li^+Fl^- was estimated to be 2.48×10^4 cm^2 mol^{-1} at 301 nm. The corresponding value for fluorene at the same wavelength is 9.4×10^3 cm^2 mol^{-1}. The results of the kinetic studies are summarised in Table 3. The difference between the results obtained by monitoring the disappearance of fluorene and that of Li^+DPP^- is most probably due to the difficulty of accurately deconvoluting the overlapping spectra of fluorene and Li^+Fl^-.

TABLE 3

Rate constants for the reaction of Li^+DPP^- with fluorene in DMTHF at 23 °C

$10^4 \times [Li^+DPP^-]$ / mol l^{-1}	$10^3 \times$ [fluorene] / mol l^{-1}	Rate constant $\times 10^3$ / l mol^{-1} s^{-1}
37.3 [a]	2.19	2.0
3.76 [b]	5.07	6.8
3.74 [b]	5.16	8.6

[a] Reaction studied by monitoring the disappearance of fluorene in a 0.01-cm cell. [b] Reactions studied by monitoring the disappearance of Li^+DPP^- in a 0.1-cm cell.

The reaction of Na^+DPP^- with fluorene in DMTHF was very fast and had to be studied by the same experimental procedure employed for Na^+DPP^- in THF. Because of problems encountered in determining the extinction coefficient of Na^+DPP^-, the results shown in Table 4 were calculated on the assumption of the plausible value 5.0×10^4 cm^2 mol^{-1} at 513 nm. The near coincidence of the two rate constants is doubtless fortuitous in view of the experimental difficulties. The value of the rate constant is sensitive to the value of ε selected: for example, changing ε to 5.7×10^4 or 4.4×10^4 cm^2 mol^{-1} alters the rate constant to 175 or to 220 l mol^{-1} s^{-1} respectively.

TABLE 4

Rate constants for the reaction of Na^+DPP^- with fluorene in DMTHF at 23 °C

$10^4 \times [Na^+DPP^-]$ / mol l^{-1}	$10^4 \times$ [fluorene] / mol l^{-1}	Rate constant / l mol^{-1} s^{-1}
1.86	4.01	194
1.68	3.52	195

At this stage the interpretation of the kinetic results is obscure. Comparing rate constants in THF for Li^+DPP^-, which is entirely present as the loose ion-pair, with those for Na^+DPP^-, 80% of which is present as the tight ion-pair, might suggest that tight ion-pairs are roughly 3 000 times more reactive than loose ion-pairs. However, although Li^+DPP^- is solely present as a tight ion-pair in DMTHF it reacts two orders of magnitude *slower* than the same compound in THF. The difference

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[14] J. H. Flynn, U.S. Department of Commerce, N.B.S. Report PB 161563, 1960.

between the dielectric constants of these two solvents is much too slight to account for this difference. Even more remarkable is the difference in the rate constants for Li^+DPP^- and Na^+DPP^- in DMTHF. Both solutes are present exclusively as tight ion-pairs, yet the latter solute has a rate constant some 30 000 times greater than the former.

The position of the absorption maximum of an ion-pair is strongly dependent upon the interionic separation, the tightest ion-pairs absorbing at the shortest wavelengths. It is clear that of the three ion-pairs so far discussed, the interionic separations of Na^+DPP^- in THF ($\lambda_{max.}$ 524 nm) and in DMTHF ($\lambda_{max.}$ 513 nm) are similar, but greater than that of Li^+DPP^- in DMTHF ($\lambda_{max.}$ 480 nm). One feature of Li^+DPP– in DMTHF which might be significant is that it is present in an unusually tight form.[9] At lower temperatures a thermodynamically distinct less-tight ion-pair is formed ($\lambda_{max.}$ 524 nm) in addition to the loose ion-pair ($\lambda_{max.}$ 560 nm). If the less-tight ion-pair has a reactivity resembling Na^+DPP^- in THF or DMTHF, then lowering the temperature of the reaction mixture would *increase* the reaction rate if the increasing mole fraction of the less-tight ion-pair more than compensated for the decrease in its rate constant. A very similar situation causes the propagation of polystyrylsodium to exhibit a negative Arrhenius activation energy.[15] Qualitative investigation of the system Li^+DPP^- fluorene in DMTHF in the range 23 to −35 °C showed, however, that the rate of reaction fell monotonously with decreasing temperature. Evidently, either the less-tight ion-pair is not highly reactive, or alternatively an insufficient mole fraction of it was present in the range of temperature studied.

When THF is added to Li^+DPP^- in DMTHF, the absorption maximum of the tight ion-pair progressively shifts from 478 nm to a limit at *ca.* 525 nm, indicating a systematic change in the composition of the solvation shell of the cation and a corresponding decrease in the tightness of the ion pairing. In addition, the presence of the loose ion-pair ($\lambda_{max.}$ 560 nm) begins to become evident at ambient temperatures at *ca* 12% (v/v) THF. A similar relaxation in the tightness of the ion pairing is observed as the temperature is reduced. Thus, the absorption maximum of the tight ion-pair in a 12% THF solution is located at 494, 503, and 506 nm at 30, 15, and 0 °C respectively. A reaction mixture was prepared with a sufficient excess of fluorene to ensure pseudo-first-order kinetics, thus facilitating the determination of rate constants (Table 5). The reaction was observed for some time at 33 °C and then the thermostat temperature was reduced in steps, yielding a series of rate constants for the same mixture. Finally the temperature was restored to 33 °C. It was found that the first and final stages at 33 °C were described by the same rate constant. Analysis of the results of Table 5 gives the approximate Arrhenius parameters $E_A = 48$ kJ mol^{-1} and $A = 8 \times 10^6$ l mol^{-1} s^{-1}.

TABLE 5

Rate constants for the reaction of Li^+DPP^- with fluorene in DMTHF containing 12% (v/v) THF

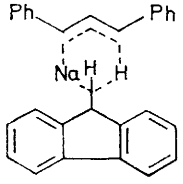
$[Li^+DPP^-] = 3.71 \times 10^{-4}$ mol l^{-1} [Fluorene] $= 5.07 \times 10^{-3}$ mol l^{-1}

t/°C	33.0	32.0	27.0	0
10^2 × rate constant/ mol^{-1} s^{-1}	5.50	4.55	4.08	0.56

The second-order rate constant at 23 °C was calculated as 2.8×10^{-2} l mol^{-1} s^{-1}, a value very similar to that obtained in DMTHF in the absence of added THF. Evidently, the change in the composition of the solvation shell revealed spectroscopically is not reflected in the kinetics.

In a final attempt to find a highly reactive tight ion-pair of Li^+DPP^-, 2,3-dihydropyran was selected from a list of some 30 solvents previously studied qualitatively. This was the only solvent which gave a stable tight ion-pair absorbing at relatively long wavelength (493 nm). The result of one simple experiment was sufficient to show that the rate constant was again very similar to that of Li^+DPP^- in DMTHF: a reaction mixture in which $[Li^+DPP^-]$ was 6.73×10^{-4} mol l^{-1} and [fluorene] was 5.27×10^{-3} mol l^{-1}, a rate constant of 1.1×10^{-2} l mol^{-1} s^{-1} was found at 33 °C. Lowering the temperature caused a monotonous decrease in reaction rate to virtually zero at the lowest temperature studied (−44 °C).

One cause of the low reactivity of Li^+DPP^- in the weaker ethers not hitherto considered is the possibility of the ion-pairs forming dimers or higher aggregates. If such aggregates were unreactive towards fluorene, then the protonation of the ion-pairs could involve one of two situations: (a) a steady state concentration of ion-pairs or (b) the dis-aggregation reaction becoming the rate-determining step. The great similarity of the rate constants for protonation in DMTHF, mixed DMTHF–THF, and dihydropyran demands an accidental similarity of an improbable number of individual steps to conform with situation (a). Case (b) cannot be excluded on these grounds, but investigation failed to reveal any concentration dependence of the spectrum of Li^+DPP^- in these solvents. Finally, the occurrence of extensive association in 10^{-4} molar ethereal solutions is without precedent.



SCHEME 3

The nature of the transition state must, of course, remain a matter for speculation. However, one likely possibility is that cation and proton are exchanged simultaneously by way of a complex such as that shown in Scheme 3. For all the systems studied in the present work, the ratio of tight to loose ion-pairs of the reactant

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[15] T. Shimomura, K. J. Tolle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 1967, **89**, 796.

is very similar to that of the product and in a favourable case (the highly reactive Na^+DPP^- in either THF or DMTHF) the transition state would involve little, or no solvation change. It is possible that the reaction of the loose ion-pair may involve some desolvation in the transition state, whereas in the case of the tight ion-pairs of Li^+DPP^- (in DMTHF and DHP) charge separation (increase of the interionic distance) may be necessary. A test of these hypotheses will require the development of more sophisticated apparatus to determine all the Arrhenius parameters.

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