Reactivities of Free Ions and Crown Ether-complexed Ion Pairs in the Protonation of Fluorenylsodium by 9-Methylfluorene

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The mechanism of the proton abstraction reaction between 9-methylfluorene and fluorenylsodium or its complex with dimethyldibenzo-18-crown-6 was studied spectrophotometrically in tetrahydropyran (THP), 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF). Ion pairs as well as free carbanions participate in the reaction. Their rate constants and the equilibrium constant of the reaction were determined. The rate constant of the free ions increases from 85 in THF to 1 300 l mol^{-1} s^{-1} in THP. These values are much higher than the rate constants for the tight ion pairs or those for DME- or crown-complexed loose ion pairs, all of which are equal or less than 2 l mol^{-1} s^{-1}. The equilibrium constant varies between 1 and 2.4 depending on the solvent and structure of the ion pair.

The reactivity of nucleophiles such as carbanions or radical anions can be drastically affected by the counterion, changes in solvent polarity, or addition of cation-chelating ligands.[1-5] Changes in the structure of the reacting ionic species are frequently the cause of the observed reactivity pattern. Numerous studies have demonstrated that formation of tight or loose ion pairs on associating a nucleophile with its counterion can either enhance or reduce its activity depending on the nature of the reaction. For example, free ions or loose ion pairs are usually more reactive than tight ion pairs in the anionic polymerization of styrene or other vinyl monomers [1,6] or in the protonation of polystyryl salts by hydrocarbons such as triphenylmethane.[7] On the other hand, protonation of carbanions or radical anions by water or alcohols is slowed down when the interionic ion pair distance is enlarged by cation solvation.[8,9] The same is observed when fluorenyl salts are added to ethylene oxide.[3,10,11] Large solvent and counterion effects have also been reported in disproportionation reactions with radical anion salts [12] and in the equilibrium addition reaction of the 9-methylfluorenyl anion to 1-phenyl-1-(4-pyridyl)ethylene.[13]

Protonation of carbanions for establishing kinetic and equilibrium acidities of conjugated hydrocarbons as well as solvent and counterion effects on this parameter have been studied extensively by Bordwell, Cram, Ritchie, Streitwieser, and other investigators.[14] Ritchie [15] reported protonation rate constants for several carbanions in methanol and dimethyl sulphoxide under conditions where the free carbanion is the stable species. It is well recognized that ion pairing and ion pair aggregation as well as ligand interaction with ion pairs can significantly modify p*K* values of acids in low polarity media such as ethereal solvents,[1,3,16] However, there is generally a scarcity of data on the effect of ion pairing or ligand complexation on the rate constants of protonation of carbanions by carbon acids.

Previous work on the properties of fluorenyl ion pairs and their crown ether complexes [2] induced us to study their reactivities in protonation reactions. The fluorenyl salts are well suited for such studies since information on ion pair structures is available from optical, conductance, and n.m.r. measurements.[2] Earlier investigations on the protonation of fluorenyl salts by benzofluorenes revealed some peculiar counterion and solvent effects on the rate constants.[17] The present study deals with the protonation of fluorenylsodium by 9-methylfluorene in ethereal solvents in the presence and absence of dimethyldibenzo-18-crown-6. The 9-methyl derivative of fluorene is only slightly more acidic than fluorene itself, and its reaction with the fluorenyl carbanion is slow enough to be carried out by a conventional batch technique. The structure of the fluorenylsodium ion pair was varied by a judicious choice of solvents and by adding the crown compound which forms a crown-complexed separated ion pair. The results show an unusual low reactivity of this ion pair compared with the free carbanion.

Experimental

Materials.—Fluorenylsodium was prepared by addition of a slight excess of recrystallized fluorene to a tetrahydrofuran (THF) solution of the sodium dicarbanion salt of 1,1-diphenylethylene.[18] The conversion is complete when the deep red colour of the dianion (*ca.* 5×10^{-2}M) changes into orange, the colour of the fluorenyl salt. The solution was evaporated to dryness and the solid fluorenylsodium recrystallized from toluene containing 5% THF. The orange needles of fluorenylsodium were filtered off, washed with toluene, and dissolved in THF. The concentrated solution was stored in a freezer. Solutions in tetrahydropyran (THP) and 1,2-dimethoxyethane (DME) were obtained from the THF stock solution by evaporation of THF and replacement of it by THP and DME, respectively. All manipulations, including the synthesis and recrystallization of fluorenylsodium, were carried out under high vacuum. Solvents were purified in the usual manner.[19] Dimethyldibenzo-18-crown-6 was synthesized in our laboratory [20] and complexed to fluorenylsodium by adding a small excess of the crown compound to the carbanion salt. Complete conversion into the crown-complexed fluorenylsodium salt was ascertained from the optical spectrum of the carbanion.[20] 9-Methylfluorene was previously obtained from Aldrich and recrystallized from hexane.

Kinetic Measurements.—Reaction rates were obtained in an all glass-enclosed evacuated apparatus details of which have been reported elsewhere including precautions which must be taken to obtain reliable kinetic data.[21] After measuring the fluorenylsodium concentration (or its crown complex), a known quantity of solid 9-methylfluorene was dissolved by distilling part of the solvent from the carbanion solution onto the solid hydrocarbon. The solutions, after thermal equilibration, were then rapidly mixed and the mixture transferred, to an attached optical cell. The cell was quickly placed in the cell compartment of a Cary 14 spectrophotometer and the change in absorbance as a function of time measured at the absorption maximum of either the fluorenyl carbanion or that of the 9-methylfluorenyl salt. The time elapsing between mixing and the first absorbance measurement could be kept to <10 s.

Reactions were monitored until equilibrium was reached, that is, until no change in optical spectrum could be detected. From this optical spectrum the equilibrium constant, K, of the proton abstraction reaction was determined. Equilibrium concentrations of the two carbanions were calculated by using the known spectra of the fluorenyl and 9-methylfluorenyl salt or their crown complexes. Since no fluorene is present at the start of the reaction, its equilibrium concentration equals that of 9-methylfluorenyl. The concentration of 9-methylfluorene is equal to the initial concentration of this hydrocarbon minus the concentration of 9-methylfluorenyl.

Results and Discussion

The proton abstraction reaction (1) between 9-methylfluorene and fluorenylsodium in ethereal solvents is complicated by the

$$\mathrm{Fl^-Na^+} + \text{9-MeFlH} \rightleftharpoons \mathrm{FlH} + \text{9-MeFl}^-\mathrm{Na^+} \quad (1)$$

fact that the dissociation constants of the two carbanion pairs are not identical. Moreover, the fraction of loose ion pairs which usually have much higher dissociation constants than tight ion pairs can also differ substantially, *e.g.*, 0.15 for 9-MeFl$^-$Na$^+$ and 0.05 for Fl$^-$Na$^+$ at 25 °C in THF as solvent. Our results (see below) show that the free carbanion is much more reactive than the carbanion pairs. Hence, the increase in the fraction of free Na$^+$ ions generated on formation of a carbanion salt that is more dissociated than the reactant carbanion salt will retard the proton abstraction reaction. This was also the case in the reaction of polystyryl salt with triphenylmethane.[7] Therefore, we only determined initial rate constants. The initial proton abstraction rate is given by equation (2) where the concentration subscripts refer to

$$(\mathrm{d[Fl^-Na^+]/d}t)_{t\,=\,0} = k_{\mathrm{obs}}\,[\mathrm{Fl^-Na^+}]_0[\text{9-MeFlH}]_0 \quad (2)$$

initial concentrations and k_{obs} indicates that more than one kind of ionic species (ion pairs and free ions) may be involved. It can be easily verified that the initial observed rate constant is given by expression (3) where l is the cell length, $(\mathrm{d}A/\mathrm{d}t)_0$

$$k_{\mathrm{obs}} = \frac{(\mathrm{d}A/\mathrm{d}t)_0 l}{[\mathrm{Fl^-Na^+}]_0[\text{9-MeFlH}]_0\,(\varepsilon - \varepsilon')}$$

denotes the initial slope of the absorbance *versus* time plot, and ε and ε′ are the respective molar absorptivities of fluorenylsodium and its 9-methyl derivative (or their crown complexes) at the wavelength of the measurement (usually the absorption maximum of the carbanion reactant).

Reaction (1) was investigated as a function of the initial concentrations of Fl$^-$Na$^+$ and 9-MeFlH in the solvents THP, THF, and DME, both in the absence and presence of dimethyldibenzo-18-crown-6. In the first two solvents, at 25 °C, the two carbanion salts are predominantly tight ion pairs, the main absorption maximum for Fl$^-$Na$^+$ being 354 nm in THP (ε 12 000) and 357 nm in THF (ε 10 800) while that of the methyl salt is 371 nm in both THP and THF (ε 10 500). The salts are loose ion pairs in DME, $\lambda_{\mathrm{max.}}$ being 373 nm for Fl$^-$Na$^+$ (ε 9 500) with a small fraction of tight ion pairs, and 388 nm for 9-MeFl$^-$Na$^+$. The spectra of the crown complexes of the carbanion salts are that of crown-complexed loose ion pairs, with no evidence for crown-complexed tight ion pairs which have been found for other crown-fluorenyl salt complexes.[22] The absorption maxima are at 373 nm (ε 14 400) for the crown complex of Fl$^-$Na$^+$ and 388 nm (ε 13 000) for that of 9-MeFl$^-$Na$^+$.

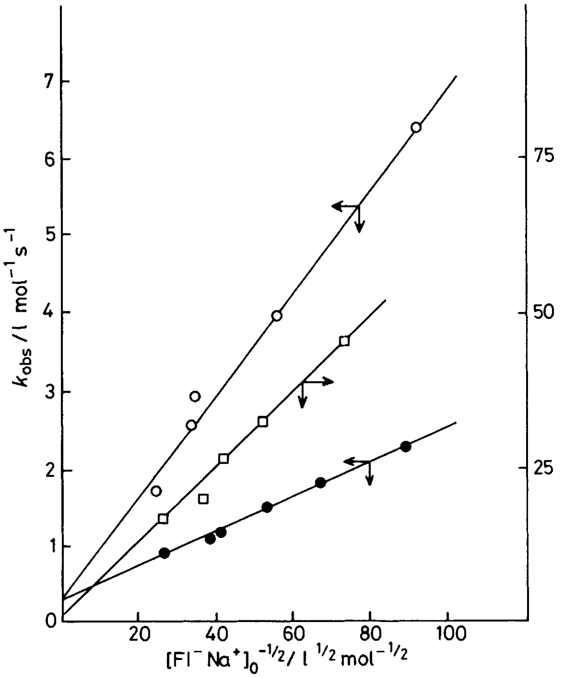

Figure 1. Observed rate constant of protonation of fluorenylsodium by 9-methylfluorene. Dependence on total carbanion salt concentration. Solvent: ○, THF; ●, THP; □, DME; 25 °C

The observed rate constants were found to be independent of the concentration of 9-methylfluorene over at least a tenfold concentration range, but the values in all systems increased on lowering the concentration of Fl$^-$Na$^+$. The proton abstraction rate also decreased on addition of sodium tetraphenylborate, a salt frequently added to suppress free ion dissociation of carbanion salts.[23] Both observations parallel those found in the anionic polymerization of styrene[23] or the proton abstraction reaction between polystyryl salts and triphenylmethane,[7] and suggest the presence of reactive free carbanions. In such a case, k_{obs} is given by equation (4)

$$k_{\mathrm{obs}} = k_{\mathrm{i}} + (k_{\mathrm{f}} - k_{\mathrm{i}})K_{\mathrm{d}}^{1/2}[\mathrm{Fl^-Na^+}]_0^{-1/2} \quad (4)$$

where K_{d} is the dissociation constant of Fl$^-$Na$^+$ or its crown complex in the respective solvents and k_{i} and k_{f} are the ion pair and free ion rate constants for the proton abstraction reaction.[23] It is assumed in the derivation of (4) that under the experimental conditions the degree of dissociation does not exceed 0.1, so that [Fl$^-$Na$^+$] can be replaced by the total carbanion concentration.

Plots of k_{obs} *versus* $[\mathrm{Fl^-Na^+}]_0^{-1/2}$ are depicted in Figures 1 and 2. The observed linear relationships support the proposed mechanism of ion pairs and free ions. It should be stressed that reproducible rate data could only be obtained when the fluorenylsodium prepared from the dianion of 1,1-diphenylethylene was carefully recrystallized (see Experimental section). This removes any excess of fluorene or ionic impurities that may interfere with the reaction. The slopes of the plots yield the free ion rate constants since K_{d} values for all systems have been reported in the literature (see Table). The ion pair rate constants, k_{i}, can be obtained from the intercepts of the least-square lines, but their reliability is not better than a factor of 1.5—2.0. However, in spite of the uncertainty in k_{i}, their values for both the tight Fl$^-$Na$^+$ ion pairs (THP, THF) and those of the DME- and crown-complexed loose ion pairs are much lower than the free ion rate constants. All pertinent

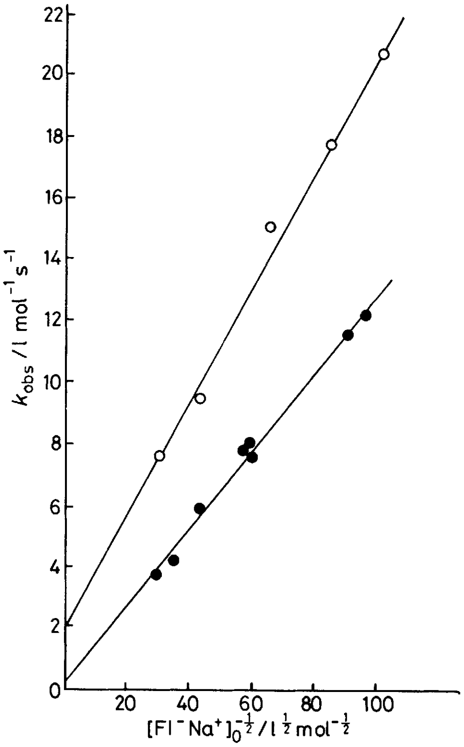

Figure 2. Observed rate constant of protonation of the dimethyldibenzo-18-crown-6 complex of fluorenylsodium by 9-methylfluorene. Dependence on total concentration of carbanion salt. Solvent: ○, THF; ●, THP; 25 °C

Ion pair (k_i) and free ion (k_f) rate constants, and equilibrium constants (K) for the protonation of fluorenylsodium and its dimethyldibenzo-18-crown-6 complex by 9-methylfluorene at 25 °C

Solvent	10^7 K_d [a]/ mol l^{-1}	k_i/ l mol^{-1} s^{-1}	k_f/ l mol^{-1} s^{-1}	K
THP	0.0031	0.25	1 300	1.04 ± 0.05
THP–crown	0.40	<0.5	600	1.6 ± 0.4
DME	55	~1.5	270	2.4 ± 0.3
THF	6.2	0.25	85	0.95 ± 0.1
THF–crown	38	2.0	90	1.5 ± 0.4

[a] K_d values taken from refs. 18, 24, and 25.

data are collected in the Table, including the equilibrium constants, K, of reaction (1).

The variation in the equilibrium constant K (see Table) as a function of solvent or ligand is not surprising. Each K value is an average value derived from a series of experiments at different carbanion concentrations, that is, at different fractions of free carbanions. The ratio of the K values for free ions and ion pairs for reaction (1) is equal to the ratio of the ion pair dissociation constants of 9MeFl$^-$Na$^+$ and Fl$^-$Na$^+$.[14] Since K_d for the former carbanion salt is higher than for the latter,[26] the presence of free ions will increase the apparent K. Also, different fractions of loose or tight ion pairs will affect K. The ratio of K values for loose and tight ion pairs in reaction (1) equals the ratio of the constants governing the tight–loose ion pair equilibria for 9MeFl$^-$Na$^+$ and for Fl$^-$Na$^+$.[14] This equilibrium constant is again higher for the 9-methyl salt than for Fl$^-$Na$^+$ itself. Generally, a hydrocarbon producing ion pairs which are more strongly associated with solvent or chelating agents is more acidic in that solvent or on adding the solvating agent.[14] Calculations of K are also complicated by differences in molar absorptivities between tight ion pairs, solvent- or crown-complexed separated ion pairs, and free ions. Since under our experimental conditions all three species may be present for both carbanion salts, the uncertainty in the K values is probably as high as 20%. The results show that for tight ion pairs (THP and THF) the pK values of fluorene and 9-methylfluorene are nearly identical, K being close to unity. The 9-methyl derivative becomes more acidic when loose ion pairs are the predominant species (DME, crown complexes). The higher acidity of 9-alkylfluorenes is well documented. For example, the ΔpK between the two hydrocarbons is 0.6 in cyclohexylamine using cesium cyclohexylamide as the base.[14]

The crown ether is not expected to interact with the free carbanion. Hence, whether derived from experiments with Fl$^-$Na$^+$ or from its crown complex, the free ion rate constant k_f should be the same as long as the same solvent is used. It is gratifying to find that this is indeed the case in THF as solvent. The k_f values are 85 and 90 l mol^{-1} s^{-1}, respectively, although the dissociation constants K_d used in calculating k_f from the slopes of the plots of Figures 1 and 2 differ by more than a factor of six (Table). The agreement is less satisfactory in THP, where the discrepancy between the two k_f values (600 and 1 300 l mol^{-1} s^{-1}) amounts to a factor of two. In this solvent the dissociation constant for the Fl$^-$Na$^+$–crown complex is 130 times that of Fl$^-$Na$^+$ itself. The latter was reported by two laboratories to be 3.1×10^{-10} mol l^{-1},[24,25] but the value of 4×10^{-8} mol l^{-1} for the crown complex may be less accurate. The Fuoss conductance plot from which this dissociation constant was calculated is strongly curved and suggests formation of triple ions.[25] Moreover, self-aggregation of these fluorenyl–crown complexes has been observed in ethereal solvents, especially when the dielectric constant decreases.[27] Both deviations will affect conductance and rate measurements, and could account for the discrepancy in k_f.

The free ion rate constants increase with decreasing dielectric constant of the reaction medium: THF < DME < THP. This is consistent with the classical theory of solvent effects on reaction rates between free ions and neutral molecules, barring any specific ion–solvent interactions.[28] The effect in this proton transfer reaction appears to be considerably larger than found in the anionic polymerization of styrene. Homopropagation rate constants for the free polystyryl carbanions (in the order of 10^5 l mol^{-1} s^{-1} at 25 °C) differ by not more than a factor two in solvents such as THF, 2-MeTHF, THP, DME, and oxepan.[29,30] More extensive desolvation requirements for the proton transfer reaction in passing from reactant to transition state could account for the stronger solvent effect. Specific effects may play a role in other solvents. For example, the k_f for reaction (1) in DMSO is 1 600 l mol^{-1} s^{-1} compared with 85 in THF in spite of the higher dielectric constant of DMSO.[31] Clearly, a more systematic study over a wider range of solvents is needed to arrive at a better understanding of solvent effects on the free ion reactivities in these carbon acid reactions.

The surprising result of these studies is the low reactivity of crown-complexed separated ion pairs in THP and THF and of loose ion pairs in DME in comparison with the reactivity of the free ion. Depending on the strength of the carbanion–cation interaction, tight carbanion pairs are weaker nucleophiles than loose ion pairs or free ions. Unless the cation catalyses the reaction (for example, in the protonation of carbanion salts by alcohols, or the nucleophilic cleavage of epoxides [3]) the tight ion pair is expected to be the less reactive species. This is found in the anionic polymerization of styrene. The reactivity of the loose ion pair in the latter reaction varies considerably. For example, the propagation rate constant for loose ion pairs of polystyryl is *ca.* 30 000 in THF and 20 000 l mol^{-1} s^{-1} in DME, while that of a glyme-separated ion pair in THF is only 3 900 l mol^{-1} s^{-1}.[32] This compares with a free ion rate constant of *ca.* 60 000 l mol^{-1} s^{-1}. The rate constants of tight ion pairs are lower by three or four powers of ten.[32]

For fluorenylsodium, the solvent- or crown-co-ordinated cation is located above the planar fluorenyl ring.[20] Conductance data suggest that the interionic distance of a crown-separated ion pair may be considerably less than that of a THF-separated ion pair. For example, the dissociation constants of Fl^-Na^+ and its dimethyldibenzo-18-crown-6 complex in THF at -60 °C are 4.0×10^{-5} and 0.33×10^{-5} mol l^{-1} although the spectra of the two ion pairs are identical to that commonly found for a loose fluorenyl ion pair.[25] Hence, part of the rather low reactivity of the crown-complexed ion pairs may result from a stronger cation–carbanion interaction, although the DME-separated ion pair also has a low reactivity.

It is possible that the solvated or crown-complexed cation prevents a close encounter between the reactive centres of the hydrocarbon and the carbanion. If the cation is above the plane of the carbanion, an approach of the hydrocarbon from below the plane would be unhindered but the proton transfer would separate the cation from the new carbanion which is energetically unfavourable. An approach of the hydrocarbon from the side of the carbanion where the cation is located would require the latter to move away from the negative charge before proton transfer can take place. Hence, the presence of a solvated or crown-complexed cation may considerably slow down the reaction and as a result low ion pair rate constants are found.

Although crown ethers frequently are excellent anion activating catalysts, in the above reaction the crown ether is not very effective in enhancing the reactivity of the ion pairs. This catalytic effect appears to be mainly limited to increasing the fraction of reactive free carbanions.

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References

1 M. Szwarc, 'Ions and Ion Pairs in Organic Reactions,' Wiley-Interscience, New York, (*a*) vol. 1, 1972; (*b*) vol. 2, 1974.
2 J. Smid, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 112.
3 T. E. Hogen Esch, *Adv. Phys. Org. Chem.*, 1977, **15**, 153.
4 J. Smid, 'Ions and Ion Pairs and Their Role in Chemical Reactions,' IUPAC Symposium, Pergamon Press, Oxford, 1979.
5 J. Smid in 'Anionic Polymerization,' ed. J. E. McGrath, ACS Symposium Series, No. 166, American Chemical Society, Washington, D.C., 1981, ch. 6.
6 T. Shimomura, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 1967, **89**, 5743.
7 L. L. Chan and J. Smid, *J. Phys. Chem.*, 1972, **76**, 695.
8 A. Rainis, R. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, 1973, **95**, 659.
9 B. Bockrath and L. M. Dorfman, *J. Am. Chem. Soc.*, 1975, **97**, 3307.
10 C. J. Chang, R. F. Kiesel, and T. E. Hogen Esch, *J. Am. Chem. Soc.*, 1973, **95**, 8446.
11 D. Lassalle, S. Boileau, and P. Sigwalt, *Eur. Pol. J.*, 1977, **13**, 599.
12 G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, 1976, **98**, 4211.
13 C. J. Chang and T. E. Hogen Esch, *Tetrahedron Lett.*, 1976, **323**.
14 M. Szwarc, A. Streitwieser, and P. C. Mowery, ref. 1*b*, ch. 3.
15 C. D. Ritchie, *J. Am. Chem. Soc.*, 1969, **91**, 6749.
16 Y. Karasawa, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, 1971, **93**, 4614.
17 T. E. Hogen Esch and J. Smid, *J. Am. Chem. Soc.*, 1967, **89**, 2764.
18 T. Ellingsen and J. Smid, *J. Phys. Chem.*, 1969, **73**, 2712.
19 T. E. Hogen Esch and J. Smid, *J. Am. Chem. Soc.*, 1966, **87**, 307.
20 K. H. Wong, G. Konizer, and J. Smid, *J. Am. Chem. Soc.*, 1970, **92**, 666.
21 T. Shimomura, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 1967, **89**, 796.
22 U. Takaki, T. E. Hogen Esch, and J. Smid, *J. Am. Chem. Soc.*, 1971, **93**, 6760.
23 D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 1965, **69**, 612.
24 S. Boileau and P. Hemery, *Electrochim. Acta*, 1976, **21**, 647.
25 T. E. Hogen Esch and J. Smid, *J. Phys. Chem.*, 1975, **79**, 233.
26 G. Collins and J. Smid, *J. Am. Chem. Soc.*, 1973, **95**, 1503.
27 U. Takaki, T. E. Hogen Esch, and J. Smid, *J. Phys. Chem.*, 1972, **76**, 2152.
28 K. J. Laidler and H. Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303.
29 M. Szwarc, 'Carbanions, Living Polymers and Electron Transfer Processes,' Wiley-Interscience, New York, 1968, p. 421.
30 L. L. Bohm and G. V. Schultz, *Makromol. Chem.*, 1972, **142**, 5.
31 C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, 1968, **90**, 3415.
32 M. Szwarc, ref. 1*b*, ch. 4.

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