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The Reactivity of Carbanions

A.A.Solov'yanov and I.P.Beletskaya

Ionic species involved in the reactions of alkali and alkaline-earth metal salts of CH-acids with various electrophiles are discussed, as well as the factors influencing the relative concentrations of these species. The reactivities of carbanions and their ion-pairs in nucleophilic substitution and addition and in electron and proton transfers are examined in terms of quantitative experimental results. A list of 140 references is included.

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I. INTRODUCTION

Many reactions of organic compounds involve carbanions, negatively charged species in which the charge—more often part of the charge—is concentrated on the carbon atom. It is now well known that the mechanism, the stereochemical direction, and the kinetics of these reactions are determined by the reactivities of the diverse forms in which carbanionic species exist in solution, as well as by their relative concentrations. However, although considerable progress has been made in studying the physical properties of ionic species, the state of information on their reactivity is still unsatisfactory.

The main purpose of the present Review is to analyse kinetic data obtained for the reactions of CH-acid salts of alkali and alkaline-earth metals, since they are almost the only sources of carbanions that have been studied in this respect. These salts have ionic structures (organolithium compounds form an exception, for the carbon–lithium bond in them is not always ionic in character[2]): i.e. they are ionophores[1], the ionic species of which exist in steady concentrations in solution, which considerably facilitates kinetic analysis.

We shall disregard the reactions of ambident anions, which develop a dual reactivity, for they have been discussed quite thoroughly[3-6]. The section on proton-transfer reactions leaves out of consideration investigations on kinetic acidity in isotope-exchange reactions in CH-acids, processes which have been discussed in sufficient detail[7-10]. Furthermore, the reactivities of carbanions are assessed from their rates of formation, which is not altogether correct, owing to the occurrence of a recovery stage that cannot be strictly allowed for, quite apart from the possible participation of both free ions and ion-pairs in these reactions, whose contributions have not been separated.

The fundamental studies by Cram showed that the character of the carbanionic species involved in isotope exchange has a decisive influence on the stereochemical result of the reaction. However, the absence of accurate kinetic parameters for each ionic species compels us to exclude the stereochemistry of the reactions of carbanions from consideration.

II. TYPES OF REACTIVE SPECIES

The complicated character of the problem of determining the reactivity of carbanions lies in the existence of their source compounds in solution not only as free ions C^- and M^+ but also as contact or solvent-separated ion-pairs C^-M^+ or $C^- \| M^+$, aggregates of ion-pairs $(C^-M^+)_n$ or $(C^- \| M^+)_n$, and more complex ionic structures, e.g. $(C^-)_{n-1}(M^+)_n$ and $(C^-)_n(M^+)_{n-1}$. In general these species differ in reactivity, which suggests that the environment has a great influence on the rates of reactions involving a carbanion. All the ionic species are interrelated by the rapidly established equilibria

$$C^-M^+ \overset{K_1}{\rightleftarrows} C^- \| M^+ \quad (K_2,\ K_3,\ C^- + M^+) \tag{1}$$

$$n\,(C^-M^+) \rightleftarrows (C^-M^+)_n \quad (C^- + (C^-)_{n-1}(M^+)_n;\ M^+ + (C^-)_n(M^+)_{n-1}) \tag{2}$$

$$n\,(C^- \| M^+) \rightleftarrows (C^- \| M^+)_n \quad (C^- + (C^-)_{n-1} \| (M^+)_n;\ M^+ + (C^-)_n \| (M^+)_{n-1}) \tag{3}$$

which are easily displaced in a particular direction by varying the reactant concentrations, changing the nature of the medium or its temperature, introducing unreactive ions or solvating additives, applying an external electric field, etc. These equilibria must be considered because the contributions of the above ionic species to the observed rate constant can be determined, and the factors influencing the reactivity of the carbanion revealed, only if the species actually present in solution and their concentrations are known.

1. Ion-pairs and Free Ions

The equilibrium between contact and solvent-separated ion-pairs was first investigated by Smid et al.,[11-24] who chose as model the fluorene salts of alkali and alkaline-earth metals, using mainly a simple spectral and conductometric technique. Subsequent investigations of this equilibrium in solutions of other salts of carbanions[12,25-32] and salts of radical-anions[33,34] established almost the same laws, governing the influence of the medium, the nature of the ions, and the temperature, as those discovered by Smid et al. We shall not discuss details, since numerous excellent reviews and monographs have appeared on this topic[22,33-35], but will report briefly the principal laws.

The constant K_1 depends on the structure of the carbanion, the size and charge of the cation, the nature of the solvent, and the temperature. The influence of the structure of the carbanion on the equilibrium between contact

and solvent-separated ion-pairs is determined by both electronic and steric factors. In general increase in the degree of charge delocalisation in the anion should favour the formation of solvent-separated ion-pairs. Thus in oxolan the value of K_1 for the sodium salts of 1,2- and 3,4-benzofluorenes exceeds several times that for fluorenylsodium [11]. The reason for the higher proportion of contact ion-pairs of the sodium salt of 1,3-diphenylbut-1-ene than of the sodium salt of 1,3-diphenylprop-1-ene in the same solvent is the increased effective charge on the carbanion due to the inductive effect of the methyl group [28].

The negative charge of a mesomeric anion containing a heteroatom may be concentrated mainly on this atom, with a consequent strengthening of electrostatic interaction between the oppositely charged parts of the ion-pair, which complicates their separation by the solvent. This provides an explanation of the presence solely of contact ion-pairs in solutions of alkali-metal salts of 9-cyanofluorene [36] and methyl fluorene-9-carboxylate [37] in dimethoxyethane.

Among structural factors that may influence the position of the equilibrium between the different types of ion-pairs we must include the presence at the anionic centre of substituents capable of impeding direct contact between the ions. Thus under the same conditions the proportion of solvent-separated ion-pairs is always smaller in solutions of alkali-metal salts of fluorene than in those of the corresponding salts of 9-2′-methylpentylfluorene [12].

Solvent-separated ion-pairs can be formed only in solvents that are capable of surrounding at least one of the ions with a dense solvate sheath. In the usual media (dipolar aprotic solvents, solvents of ether type) it is the metal cation in the usual ion-pairs of carbanions that interacts with the solvent. Therefore the position of the equilibrium between intimate and loose ion-pairs depends primarily on how well specifically solvated is the gegenion. In solvents of ether type (oxolan, dimethoxyethane, diethyl ether, oxan) the proportion of solvent-separated ion-pairs always increases with decrease in the radius of the alkali-metal cation in the sequence

$$Cs^+ < Rb^+ < K^+ < Na^+ < Li^+.$$

This is the situation in solutions of alkali-metal salts of fluorene [11], triphenylmethane [30], 1,3-diphenylbut-1-ene [26,28] and 1,3-diphenylprop-1-ene [27,28], indene [30], 4,5-methylenephenanthrene [32], and 1- and 2-methylnaphthalenes [31].

On passing from salts of alkali metals to those of alkaline-earth metals (difluorenyl-barium, -strontium) the proportion of solvent-separated ion-pairs diminishes considerably [13,14], as a consequence both of increase in the electrostatic interaction in salts of doubly charged cations and of the great hindrance to their solvation. Here, too, the equilibrium shifts towards solvent-separated ion-pairs with decrease in the radius of the cation [14]. Formation of solvent-separated ion-pairs is considerably favoured by increasing the polarity of the solvent and its solvating power for the cation, the latter factor often being dominant. The proportion of loose ion-pairs in alkali-metal salts of fluorene increases (i) as the solvent becomes more basic [15,16] in the sequences

dioxolan < oxan < 2,5-dihydrofuran < oxolan < oxetan,

dioxan < 3,4-dihydropyran < oxetan,

oxolan ≪ hexamethylphosphoramide, dimethyl sulphoxide

(ii) on passing from uni- to bi- and multi-dentate solvents [15,16] in the sequences

oxolan ≪ 2-methoxymethyloxolan,

m-dimethoxybenzene < oxolan < *o*-dimethoxybenzene

and (iii) with increase in the number n of oxyethylene units in glymes (dimethyl ethers of polyethylene glycols) $CH_3O[CH_2CH_2O]_nCH_3$ added in small quantities to ethereal solvents [17,18]

$$1 < 3 < 4 < 5 < 6 < 7 < 9 < 22.$$

Analogous regularities are observed on examining equilibria between ion-pairs of alkali-metal salts of 9-2′-methylpentylfluorene [12], triphenylmethane [30,38], 1,3-diphenylalkenes [25-28], and other systems [30-32].

However, the greatest effect on the equilibrium between ion-pairs is exerted by crown polyethers [39] and cryptates [40]: small additions to solutions of carbanion salts of alkali metals [19,20] or alkaline-earth metals [10] increase K_1 by several powers of ten.

Lowering the temperature causes the equilibrium between ion-pairs in solutions of carbanion salts to shift towards solvent-separated pairs in all the systems studied, since at low temperatures solvation is less disturbed by the thermal motion of the molecules. Incorporation of solvent into the ion-pair is accompanied by decreases in enthalpy and entropy. Table 1 gives some idea of the thermodynamic parameters of the transition of intimate into loose ion-pairs, as well as the magnitude of the equilibrium constants.

Table 1. Thermodynamic parameters of the equilibrium (1) between contact and solvent-separated ion-pairs at 25° C.

Anion	Solvent	Cation	K_1	$-\Delta H_1$, kcal mole^{-1}	$-\Delta S_1$, e.u.	Ref.
Fluorenyl	oxolan	Li^+	4.6	7.5	22	16
Fluorenyl	oxan	Li^+	0.45	6.6	28	16
Fluorenyl	oxepan	Li^+	0.24	4.3	16	16
9-2′-Methylpentylfluorenyl	2,5-dimethyloxolan	Li^+	50	10.0	50	12
2-Methyl-1-3-diphenylallyl	oxepan	Li^+	—	8.4	30.5	25
2-Methyl-1-3-diphenylallyl	oxolan	Li^+	—	6.7	24.5	25
2-Methyl-1-3-diphenylallyl	oxolan	Na^+	—	10.7	41	25
1,2,3-Triphenylallyl	oxepan	Li^+	—	6.0	20	25
1,2,3-Triphenylallyl	oxolan	Ba^{2+}	—	4.1	21	25
1,3-Diphenylallyl	oxolan	Na^+	—	6.1	22	27
1,3-Diphenylallyl	oxolan	K^+	—	4.1	16.5	27
Triphenylmethyl	oxolan	Na^+	0.38	8.2	28	38
Triphenylmethyl	dimethoxyethane	K^+	0.1	6.7	16	38

The dissociation equilibria—between ion-pairs and free ions (equilibrium constants K_2 and K_3)—are influenced by the same factors—structure of carbanion, size and charge of gegenion, nature and temperature of medium—as is the equilibrium between ion-pairs. These factors have considerably less influence on the dissociation of solvent-separated ion-pairs, in which interionic interaction is appreciably weaker. It must also be borne in mind that the work of diluting oppositely charged ions to an infinite distance (i.e. dissociation) is done mainly at the stage of introducing the first solvent molecule between them. It is by no means always possible to isolate the parameters relating to dissociation of ion-pairs of a certain type, since the measured dissociation constant [calculated from the Fuoss conductance equation] is a composite quantity: $K_D^{-1} = K_2^{-1} + K_3^{-1}$. Hence the enthalpy and entropy of dissociation are also composite [16]:

$$\Delta H_D = \Delta H_3 + \Delta H_1(1+K_1)^{-1}; \quad \Delta S_D = \Delta S_3 + \Delta S_1 \cdot (1+K_1)^{-1}.$$

It is not surprising, therefore, that not only K_D but also the observed values of ΔH_D and ΔS_D vary with temperature, owing to the shift in the equilibrium between the ion-pairs.

The data in Table 2 show that in the large majority of cases the enthalpy and the entropy of dissociation are negative; moreover, they usually decrease in absolute magnitude with fall in temperature. This was to be expected, since at low temperatures the terms $\Delta H_1(1+K_1)^{-1}$ and $\Delta S_1(1+K_1)^{-1}$ make smaller contributions to the observed functions. The magnitudes of ΔH_D and ΔS_D depend both on K_1 and on the thermodynamic parameters of the transition of contact into solvent-separated ion-pairs (Table 1). If ΔH_D (and of course ΔS_D also) reach limiting values unaffected by further fall in temperature[14,21], this would suggest that ion-pairs of only one type (solvent-separated) exist in solution under these conditions. If variation of the temperature does not affect the enthalpy of dissociation, this also indicates that free ions are formed from ion-pairs of a single type, but they may be either contact[14,21,36] or solvent-separated[14,16,21]. The type can be decided from the magnitudes of ΔH_D, which are higher for close ion-pairs (by factors of 2–3[14,16,21,28,41]), and also from spectral data[22].

Table 2. Parameters of the dissociation of certain salts of alkali and alkaline-earth metals with CH-acids.

Anion	Cation	Solvent*	t, °C	$10^8 K_D$, M	$-\Delta H_D$, kcal mole^{-1}	$-\Delta S_D$, e.u.	Ref.
9-Methylfluorenyl	Li^+	DME	25	380	—	—	37
9-Phenylfluorenyl	Li^+	DME	25	560	—	—	37
Fluorenyl	Li^+	DME	15	620	2.9	33	21
Fluorenyl	Li^+	DME	−65	2140	~0	—	21
Fluorenyl	Cs^+	DME	15	25	4.6	45	21
Fluorenyl	Cs^+	DME	−65	300	~1.0	—	21
Fluorenyl	Li^+	oxolan	25	300	3.5	37	21
Fluorenyl	Li^+	oxolan	−70	1550	~0	—	21
Fluorenyl	Cs^+	oxolan	25	1.4	2.9	46	21
Fluorenyl	Cs^+	oxolan	−70	5.5	1.0	38	21
Fluorenyl	Ba^{2+}	oxolan	20	5.3	10	54.4	14
Fluorenyl	Ba^{2+}	oxolan	−70	22	10	54.4	14
Fluorenyl	Sr^{2+}	oxolan	20	17.3	13.3	76	14
Fluorenyl	Sr^{2+}	oxolan	−70	256	0	25	14
Triphenylmethyl	Na^+	ether	25	$1.5\cdot10^{-4}$	—	—	41
Triphenylmethyl	Na^+	oxolan	25	760	6.2	44	38
Triphenylmethyl	Na^+	oxolan	−60	5040	0.6	23	38
Triphenylmethyl	K^+	oxolan	25	340	—	—	38
Polystyryl	Na^+	HMPA	40	10^6	—	—	42
Polystyryl	Na^+	oxolan	25	15	8.2	—	43
Polystyryl	Cs^+	oxolan	25	0.47	1.8	—	43
Tri-*p*-nitrophenylmethyl	Li^+	oxolan	25	21	—	—	44
Tri-*p*-nitrophenylmethyl	Cs^+	oxolan	25	570	—	—	44
9-Cyanofluorenyl	Li^+	DME	25	30	6.5	—	36
9-Cyanofluorenyl	Na^+	DME	25	100	3.7	—	36
9-Cyanofluorenyl	Na^+	ethanol	25	$>10^6$	—	—	45
9-Cyanofluorenyl	Cs^+	DME	25	500	4.9	—	36
Poly-2,3-dimethylbutadienyl	Li^+	oxolan	25	$\sim10^{-4}$	—	—	46
Polyisoprenyl	Li^+	oxolan	25	0.08	—	—	46
Polybutadienyl	Li^+	oxolan	25	3	—	—	46
Poly-α-methylstyryl	Li^+	oxolan	25	8.3	—	—	46
Polystyryl	Li^+	oxolan	25	35	—	—	46
Cyclopentadienyl	Li^+	oxolan	25	47	—	—	46
Indenyl	Li^+	oxolan	25	990	—	—	46

*DME = dimethoxyethane; HMPA = hexamethylphosphoramide.

The thermodynamic approach to the problem of the dissociation of ion-pairs[47,48], in which the solvent is regarded as an unstructured isotropic dielectric, leads to the Denison–Ramsey equations

$$\Delta H_D = \frac{Ne^2}{a\varepsilon}\left(1+\frac{\partial \ln \varepsilon}{\partial \ln T}\right), \quad (4)$$

$$\Delta S_D = \frac{Ne^2}{a\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial T}\right) + \Delta S_T, \quad (5)$$

in which a is the distance between the ionic centres of the pair, while ΔS_T represents the increase in entropy due to the appearance of two species instead of one. Since the temperature coefficient $\partial \ln \epsilon / \partial \ln T$ is always negative, and for liquids exceeds unity in absolute magnitude[49], the values of ΔH_D and ΔS_D predicted by Eqns. (4) and (5) are also negative, in excellent agreement with experimental results. However, coincidence of calculated and experimental magnitudes of ΔH_D (and ΔS_D) is observed only when transition of the ions from the ion-pairs to the free state is not accompanied by changes in their solvent sheaths, i.e. usually on the dissociation of solvent-separated pairs[14,16,21,38], which provides a further test for the structure of the dissociating species.

Since the formation of solvent-separated from contact ion-pairs and that of free ions from both types are similar in character, ions being separated by one or more solvent molecules in both cases, they are governed by the same laws. For purely carbanionic systems the dissociation constant increases with decrease in the size of the cation[14,16,21,38,50] and with increase in its charge[14] (Table 2). However, the presence of a heteroatom in the organic anion reverses the dependence of the dissociation constant on the cationic radius[36,44] (Table 2). Transfer to a solvent possessing greater solvating power for the cation and a larger dielectric constant produces a sharp increase in the dissociation constant[38,42,44–46] (Table 2); it is probable that all three equilibrium constants—K_1, K_2, and K_3—increase. Solvating additives in the solution also increase the dissociation constant, of course[14,44]. In some cases[51] a linear correlation can be observed between the logarithm of the dissociation constant and the reciprocal of the dielectric constant of the medium.

Values of the dissociation constant may serve as a measure of the relative stabilities of the anions formed by dissociation[46,52]. The electron-donor character of methyl groups is responsible for the increase in K_D in the sequences of lithium derivatives (Table 2)[46]

poly-2,3-dimethylbutadienyl < polyisoprenyl < polybutadienyl,

poly-α-methylstyryl < polystyryl

Here the increase in stability of the anions is consistent with the fall in their reactivity[46,52]. However, such a rule would probably apply only to the dissociation of contact ion-pairs. The stability factor is less significant in the dissociation of solvent-separated ion-pairs (it affects, of course, the value of K_1). In any case, the dissociation constants of solvent-separated ion-pairs of lithium salts of substituted fluorenes are closely similar, although values of pK_a in the corresponding series of CH-acids vary by 4 units[37] (Table 2).

The dissociation constant of cyclopentadienyl-lithium is only around 5% of that of indenyl-lithium[46], although the pK_a of indene is 3.5 units higher[53]. Solutions of these salts, however, contain both contact and solvent-separated ion-pairs[30].

2. Aggregates of Ion-Pairs

The aggregation of ion-pairs (Eqns. 2 and 3) has been considerably less well studied than the equilibria between ions and ion-pairs or between contact and solvent-separated pairs, from both kinetic and thermodynamic points of view. Therefore the number of theoretical models created to describe these processes is also small: Fuoss and Kraus[54] examined the possibility of the formation of ion-triplets, and Pettit and Bruckenstein[55] that of symmetrical ion quadrupoles and sexapoles. The reason for the association of ion-pairs of carbanions is obviously dipole–dipole interaction, so that these aggregates are

usually met in media of low polarity, such as aliphatic hydrocarbons and benzene[56,57]. Association in polar media such as oxolan is usually due to special causes, e.g. difunctionality of the polymer chain[50] or a doubly charged cation[68,69]. The stability of aggregates of ion-pairs and their degree of association depend significantly on the size of the alkali-metal cation and the structure of the anion. Polystyryl-lithium in benzene, cyclohexane, toluene, and heptane[56-60] and poly-α-methylstyryl-lithium in aliphatic hydrocarbons[63] are dimerised; polyisoprenyl-lithium in heptane, toluene, and certain other hydrocarbons forms tetramers[60-62]; and polybutadienyl-lithium[60,54] forms hexamers. On passing from this last compound to polybutadienylpotassium the degree of association of the ion-pairs falls[64] from 6 to 2. In benzene polystyrylsodium is dimerised down to concentrations of $\sim 10^{-5}$ M, dimers of potassium ion-pairs break down at $\sim 10^{-3}$ M, and caesium ion-pairs do not associate at all in this solvent[65]. In cyclohexane polystyrylpotassium is slightly associated, but the rubidium and caesium salts are monomeric[67]. Additions of solvating solvents such as oxolan tend to break down association complexes of ion-pairs in hydrocarbon media[65,66].

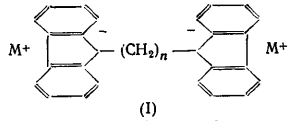
Quantitative information on the association of ion-pairs of carbanions is almost completely lacking. The equilibrium constant of the dimerisation of polystyrylpotassium is 3mM in cyclohexane at 40°C,[67] and 0.6mM in benzene at 20°C[65] ($\Delta H = 7.6$ kcal mole^{-1}).

Whereas organolithium compounds containing resonance-stabilised groups, e.g. benzyl, allyl, diphenylmethyl[56-67], associate because of dipole–dipole interaction of ion-pairs, simple alkyl-lithium compounds form aggregates with multicentre bonds[70,71] involving p orbitals. In hydrocarbons, ether, or benzene these aggregates usually comprise four[72,73] or six[74-76] monomer units. X-Ray examination indicates that tetrameric alkyl-lithium compounds have a tetrahedral structure, with lithium atoms at the corners of the tetrahedron, and alkyl groups located above the centres of the faces[72].

The association of ion-pairs of carbanions in hydrocarbons involves only the contact type. In ethers, however, solvent-separated ion-pairs also are able to associate[23]: in oxolan fluorenylsodium ion-pairs separated by a crown polyether form dimers. Increase in the dipole moment and the possibility of denser packing of ions in the dimer are probably significant here[23].

Linear carbon-chain polymers having an active centre at each end of the chain exhibit unusual behaviour. The anion formed on the dissociation of one ion-pair of difunctional polystyrylcaesium in oxolan cyclises with the ion-pair at the other end to form an intramolecular triple ion[50].

Bolaform electrolytes—caesium and sodium salts of $\alpha\omega$-difluoren-9-ylpolymethylenes

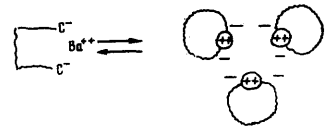


(I)

n =2, 3, 4 and 6

in oxolan—form analogous triple ions[24]. The cyclisation constant increases with the number of methylene units and on passing from sodium to caesium. Formation of cyclic triple ions of sodium salts has a very low probability because the sodium cation is well solvated by oxolan.

In oxolan polystyrylbarium associates into a trimer, forming a "rosette" (II)[68]:



II

III. KINETIC APPROACH

The observed reaction rate constant for a compound capable of existing in more than one form is a composite quantity which, provided that the rate of establishment of equilibrium between these forms greatly exceeds the reaction velocity, can be written

$$k_{obs} = \sum_i k_i \alpha_i, \qquad (6)$$

where α_i is the proportion of a given ionic species and k_i is the rate constant. Obviously, calculation of the thermodynamic activation functions from the temperature dependence of the observed rate constant may in general give incorrect results. Nor does the observed constant give a true idea of the reactivity of the ions. On the other hand, it is also clearly impossible in any case to isolate the individual rate constants k_i by means of Eqn. (6). Even in cases in which only two ionic species are in equilibrium in solution, three independent variables—the rate constants of the two species and the proportion α of one of them (the proportion of the other is $1 - \alpha$)—occur in this equation. The constants can then be determined in only one way—by varying the value of α and solving the set of linear equations

$$k_{obs} = k_1\alpha + k_2(1-\alpha) = k_2 + \alpha(k_2 - k_1). \qquad (7)$$

The rate constants can also be determined graphically, by plotting k_{obs} against α, when the slope gives the difference $k_2 - k_1$, while the intercept on the ordinate axis is k_2. When these reactive species contain different numbers of ions (e.g. an ion and an ion-pair, or an ion-pair and an aggregate of ion-pairs), the quantity α can be varied by varying the concentration. When, however, the reactive species contain the same number of ions (contact and solvent-separated ion-pairs), variation of α requires the introduction of solvating additives, which displace the equilibrium towards the species having the greater inter-ionic distance. However, this case is fraught with unpleasant consequences: firstly, free ions may be formed, i.e. yet another reactant species; and secondly, a solvent-separated ion-pair whose cation is solvated by the additive may differ in reactivity (though slightly) from an ion-pair whose cation is solvated simply by the solvent.

Obviously, it is impossible to vary the temperature or the dielectric constant of the medium, since this would entail a change in the values of the constants themselves.

Reactive systems comprising two species are among the most thoroughly studied. Many kinetic data have been assembled especially on the reactions of ionophores present in solution as an equilibrium mixture of ion-pairs and free ions. The observed rate constant for such systems can be represented by an equation suggested by Acree[77]:

$$k_{obs} = \alpha k_{ion} + (1-\alpha)k_{ip}, \qquad (8)$$

where k_{ion} and k_{ip} are the reaction rate constants of ions and ion-pairs respectively, while α is the degree of dissociation calculated from conductivity data for solutions of the ionophores. In cases in which the degree of dissociation does not exceed a few percent, it can be expressed by the equation

$$K_D = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 \quad (\alpha \ll 1) \tag{9}$$

in the form $\alpha = (K_D/C)^{1/2}$, where C is the concentration of the ionophore. Formula (8) is then transformed into the very frequently used equation[36,38,42,44,50,52,78-102]

$$k_{obs} = k_{ip} + (k_{ip} - k_{ip})\frac{K_D^{1/2}}{C^{1/2}}. \tag{10}$$

In order to evaluate k_{ip}† and k_{ion} from (10) it is sufficient to know the dissociation constant K_D. If for some reason this cannot be measured, only k_{ip} can be calculated from Eqn. (10).

The degree of dissociation α can be varied also by means of the common-ion effect, by introducing into the solution a compound that dissociates considerably better than test reagent to give one of the components (unreactive, of course) of the ion-pair. Examples of such compounds are alkali-metal tetraphenylborates[36,38,50,52], triphenylcyanoborates[42], and perchlorates[81,82]. The observed rate constant will then be given by[50,85]

$$k_{obs} = k_{ip} + (k_{ion} - k_{ip})\frac{K_D}{[M^+]}, \tag{11}$$

where $[M^+]$ is the concentration of the common ion (in the present case the cation) calculated from the dissociation constant of the additive (since only a minute proportion of the free M^+ ions in the solution results from dissociation of the reactive ionophore). Simultaneous solution of (10) and (11) enables k_{ion}, k_{ip}, and K_D to be found without the need for conductometric measurements[38,50,82]. It is possible, of course, to use[81,82,103] Eqn. (11) independently of (10).

Table 3. Estimated contributions by free ions and ion-pairs to observed rate constant.

α	k_{ion}/k_{ip}	Contributions*, %		K_D, M	c, M	α*
		free ions	ion-pairs			
0.001	10^4	91	9	10^{-10}	10^{-5}	0.003
0.001	10^3	50	50	10^{-10}	10^{-4}	0.001
0.01	10^4	99	1	10^{-10}	10^{-3}	0.0003
0.01	10^3	91	9	10^{-8}	10^{-5}	0.03
0.01	10^2	50	50	10^{-8}	10^{-4}	0.01
0.01	10	9	91	10^{-8}	10^{-3}	0.003
0.1	10^2	91	9	10^{-6}	10^{-5}	0.4
0.1	10	53	47	10^{-6}	10^{-1}	0.003

*Approximate values.

Concluding our examination of the kinetic aspect of the joint involvement of free ions and ion-pairs in a reaction, we give some estimates‡ of the contributions by these species to the observed rate constant as functions of k_{ion}/k_{ip} and α, and for clarity values of α for certain dissociation constants and concentrations of the salt most frequently met in practice (Table 3). These data lead to further conclusions: firstly, if ions and ion-pairs differ greatly (10^3–10^4) in reactivity, ions are in effect the sole reactants, even if their proportion does not exceed 1%, a situation characteristic of the reactions of many salts whose dissociation constants exceed 10^{-8} M (e.g. Table 2); secondly, the contribution by ion-pairs becomes considerable only with a relatively small difference in reactivity between the two ionic species ($k_{ion}/k_{ip} \approx 10$) and at very low degrees of dissociation, as is typical of preparative experiments, in which large reactant concentrations are used.

Aggregates of ion-pairs make hardly any contribution to the observed rate constant, so that their role is usually merely to lower considerably the concentration of reactive ion-pairs[65,67]. If the equilibrium between the ion-pairs and their association complexes is displaced towards the latter, the observed rate constant can then be expressed[104]

$$k_{obs} = K_A^{1/n} k_{ip} n^{-1/n} C^{1/n}, \tag{12}$$

where n is the association factor, K_A the association constant, k_{ip} the true reaction rate constant of the ion-pairs, and c the concentration of the reactant. The slope of the double logarithmic plot of observed rate constant against reactant concentration enables us to determine the association factor n and hence calculate the effective rate constant $k_{eff} = K_A^{-1/n} k_{ip}$[65,67,104]. If by varying the concentration we can bring the system into a region in which the equilibrium is completely displaced towards monomeric ion-pairs, the rate constant k_{ip} determined in this region (in which $k_{eff} = k_{obs} = k_{ip}$) enables us to calculate the equilibrium association constant K_A from k_{eff}[65,67,104].

The calculation is considerably more complicated in systems in which several reactive species are present[36,42,83,94], but this does not prevent determination of their reactivity, though less accurately.

IV. REACTIONS OF CARBANIONS

Reactions in which reactivities of carbanions have been studied, and various factors influencing them have been investigated, include nucleophilic substitution at a saturated carbon atom (alkylation of carbanions), nucleophilic addition (mainly polymerisation of vinyl monomers), and processes involving proton and electron transfer. These four types of reactions will be discussed below.

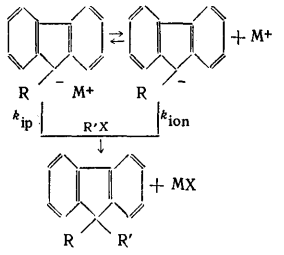
1. Nucleophilic Substitution

The reactivity of carbanions in nucleophilic substitutions has been studied only on the fluorenyl system (9-RFl$^-$M$^+$)[36,37,45,78-82,105]. However, such restriction to a single hydrocarbon has not prevented (and may have helped) establishment of the effects on reactivity of the most diverse

†The value of k_{ip} obtained from the intercept relates to all types of ion-pairs present together in the solution: i.e. it can be written in the form (6), where k_i will represent the reactivity of the ith kind of ion-pairs.

‡These estimates are valid for any pair of ionic species in equilibrium, e.g. for contact and solvent-separated ion-pairs. The only difference is that the calculation of α requires that Eqn. (9) should be replaced by a different formula, representing the given type of equilibrium.

factors—substituents at the anionic centre, the size of the alkali-metal cation, the nature of alkylating and leaving groups, the character of the solvent. The general scheme of the reactions appeared to be



(13)

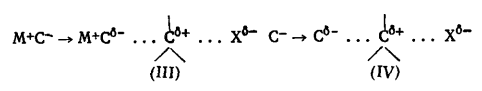
where R = H, CH_3, C_6H_5,[37,79] $SO_2C_6H_5$,[81,82] $COOCH_3$,[37,81,82] and CN[36,37,45,78,80–82,105]; $M^+ = Li^+$, Na^+, K^+, Cs^+, $(C_6H_5)_4As^+$; R′ = CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9,[36,45,78,80,105] *m*- and *p*-substituted $C_6H_5CH_2$;[105] and X = F, Cl, Br, I. The solvents used comprised alcohols, dipolar aprotic solvents, and solvents of ether type. The principal results obtained in these investigations are summarised in Tables 4–7.

Table 4. Kinetic parameters of the reaction of alkali-metal salts of 9-cyanofluorene (9-CNFl$^-$M$^+$) with alkyl halides (RX) at 25° C.

M	Solvent	RX	10^3k_{ip}, M^{-1} s^{-1}	10^3k_{ion}, M^{-1} s^{-1}	$\frac{k_{ion}}{k_{ip}}$	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Ref.
Li	DME	MeI	3.6	1750	485	—	—	36
Li	DME	EtI	2.8	81	29	—	—	36
Li	DME	PrI	1.6	28	18	—	—	36
Li	DME	PrBr	0.34	18	53	—	—	36
Li	DME	BuBr	0.019	2.7	142	—	—	36
Na	ethanol	MeI	—	144*	—	13.3	−18.7	105
Na	DME	MeI	39	1620	42	—	—	36
Na	DME	EtI	8	60	8	—	—	36, 78, 80
Na	HMPA	EtI	—	78	—	—	—	45
Na	DMAA**	EtI	—	68	—	—	—	45
Na	DMFA***	EtI	—	66	—	—	—	45
Na	DMSO****	EtI	—	48	—	—	—	45
Na	AN*****	EtI	—	20	—	—	—	45
Na	ethanol	EtI	—	13.1	—	—	—	45, 80
Na	ethanol	EtI	—	22.3*	—	14.1	−19.6	105
Na	ethanol	iso-PrI	—	8.84*	—	13.7	−22.7	105
Na	ethanol	iso-PrBr	—	2.31*	—	22.0	1.8	105
Cs	DME	EtI	11	93	11	—	—	36

*At 30.5° C.
**Dimethylacetamide.
***Dimethylformamide.
****Dimethyl sulphoxide.
*****Acetonitrile.

In all cases association of the carbanion with the cation deactivates the nucleophile: with one exception (the reaction of 9-cyanofluoren-9-ylsodium with benzyl fluoride[81,82]—Table 5) the rate constant of the free ion exceeds that of the ion-pair: i.e. $k_{ion}/k_{ip} > 1$. This was to be expected, since the activated complex formed in the reaction of the ion-pair (III) differs from that for reaction of the free carbanion (IV) (coordination of the cation M^+ with the leaving group X^- in the transition state is a special case):



The presence of the cation in (III) tends to localise the charge on the carbanion, which prevents formation of a new ethylenic bond or else increases the effective distance between the charged centres of the anion, thereby weakening the Coulombic interaction of the reactants.

Table 5. Kinetic parameters of the reactions of benzyl halides $C_6H_5CH_2X$ with alkali-metal salts of 9-substituted fluorenes (9-RFl$^-$M$^+$) in alcohols at 30° C.

X	R	M+	Solvent	k_{ip}, M^{-1} s^{-1}	k_{ion}, M^{-1} s^{-1}	$\frac{k_{ion}}{k_{ip}}$	Ref.
F	CN	Na	t-BuOH	$\sim 1.9\cdot10^{-3}$	$\sim 1.9\cdot10^{-3}$	~1	81, 82
F	SO_2Ph	Na	t-BuOH	$\sim 2\cdot10^{-3}$*	—	—	81
Cl	COOMe	Li	t-BuOH	0.185	4.27	23	81
Cl	COOMe	Na	t-BuOH	0.124	4.27	34	81
Cl	CN	Na	t-BuOH	0.20	4.1	20.5	81, 82
Cl	CN	Na	EtOH	—	0.127	—	105
Cl	COOMe	K	t-BuOH	0.097	4.27	44	81
Cl	SO_2Ph	Na	t-BuOH	~0.2*	—	—	81
Br	CN	Na	EtOH	—	6.79**	—	105
Br	CN	Na	t-BuOH	11	350	32	81, 82
Br	COOMe	Na	t-BuOH	7.76	256	33	81
Br	COOMe	K	t-BuOH	3.88	256	66	81
Br	SO_2Ph	Na	t-BuOH	~7*	—	—	—

*Observed reaction rate constant.
**At 25° C.

Table 6. Rate constants for the reactions of sodium 9-cyanofluoren-9-ide with substituted benzyl halides $YC_6H_4CH_2X$ in ethanol[105].

Y	10^2k_{ion}, M^{-1} s^{-1}		Y	10^2k_{ion}, M^{-1} s^{-1}	
	X=Br (10° C)	X=Cl (20° C)		X=Br (10° C)	X=Cl (20° C)
H	295	6.46	3-Cl	611	13.7
3-Me	527	11.9	3-Br	707	—
4-MeO	808	11.9	3-NO_2	3040	55.3
3-MeO	—	8.96			

Table 7. Influence of structure of carbanion on its reactivity during alkylation and benzylation.

System	R	10^8K_D, M	k_{ion}, M^{-1} s^{-1}	k_{ip}, M^{-1} s^{-1}	$\frac{k_{ion}}{k_{ip}}$	pK_a^*
9-RFl$^-$Li$^+$ + BuBr (DME, 25°) (Ref.37)	CN	30.1	$2.7\cdot10^{-3}$	$1.9\cdot10^{-5}$	142	8.6[37]
	COOMe	6.6	$6.7\cdot10^{-3}$	$1.0\cdot10^{-4}$	67	10.3[106]
	Ph	560	$2.2\cdot10^{-1}$	$7.4\cdot10^{-2}$	3	16.4[106]
	Me	380	20.2	6.3	3.2	19.7[106]
	H	470	21,6	9.9	2.2	20.5[106]
9-RFl$^-$Na$^+$ + $C_6H_5CH_2Cl$ (t-C_4H_9OH, 30° C) (Refs.81,82)	CN	810	4.1	0.20	20.5	11.4[108]
	COOMe	130	4.27	0.124	34	12.9[107,8]
	SO_2Ph	35	—	~0.2**	—	15.0[81]
9-RFl$^-$Na$^+$ + $C_6H_5CH_2Br$ (t-C_4H_9OH, 30° C) (Refs.81,82)	CN	810	350	11	32	11.4[108]
	COOMe	130	256	7.76	33	12.9[108]
	SO_2Ph	35	—	~7**	—	15.0[81]

*These values of pK_a were used in discussing the results in the papers cited.
**Observed reaction rate constant.

Hence the ratio k_{ion}/k_{ip} for a fixed anion structure should increase with the interaction between the ionic moieties of the pair. For contact ion-pairs the ratio may be expected to increase in the sequence $Cs^+ < K^+ < Na^+ <$

Li^+. On the other hand, on passing from contact to solvent-separated ion-pairs, in which the oppositely charged components are a long distance apart, the relative reactivity of the carbanion should decrease considerably. This is indeed the case: in the reactions of the lithium salts of fluorene and of its 9-methyl and 9-phenyl derivatives in dimethoxyethane solution, where their ion-pairs are separated by the solvent, the ratio is only $k_{ion}/k_{ip} = 2-3$[37] (Table 7).

The dependence of the ratio on the size of the cation is different in dimethoxyethane from that in t-butyl alcohol: in the ether the reactivity of the ion-pairs increases in the sequence $Li^+ < Na^+ < Cs^+$[36] (Table 4), but in the alcohol in the sequence $K^+ < Na^+ < Li^+$[81] (Table 5). However, although it can be accepted[36] that contact ion-pairs are present in dimethoxyethane, the situation in t-butyl alcohol is not altogether clear. In any case, this question has not been specially investigated[81], and the possibility of the solvation of ambident anions (as is the anion of methyl fluorene-9-carboxylate) by hydrogen bonding[107] does not exclude the presence of solvate-separated ion-pairs in solutions of the alkali-metal derivatives of this ester.

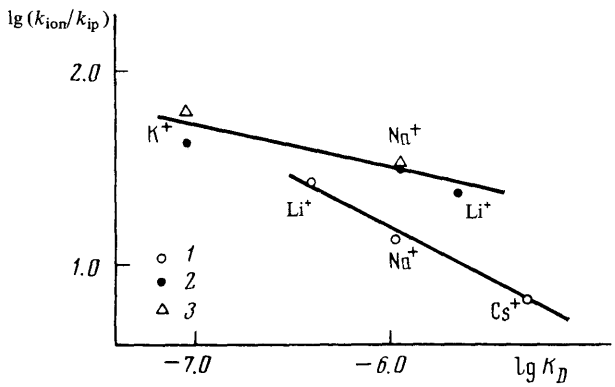


Figure 1. Correlation of relative reactivity of carbanion with dissociation constants of its ion-pairs (Tables 4 and 5): 1) C_2H_5I; 2) $C_6H_5CH_2Cl$; 3) $C_6H_5CH_2Br$.

Nevertheless, the variation of the ratio in one or other system can be predicted from the dissociation constant of the ion-pairs, the parameter which ultimately characterises their stability. Fig. 1 shows double logarithmic graphs of the dependence of k_{ion}/k_{ip} on K_D based on data obtained for the benzylation of alkali-metal salts of methyl fluorene-9-carboxylate with benzyl chloride and bromide in t-butyl alcohol and for the alkylation[36] of alkali-metal salts of 9-cyanofluorene with ethyl iodide in dimethoxyethane. In the latter case the mean value for the three salts investigated $k_{ion} = 0.078\ M^{-1}\ s^{-1}$ was used for the correlation, with a correction for the involvement of the sodium salt of solvent-separated ion-pairs[80]. The linearity of the graphs indicates the existence for these systems of a free-energy relation of the type

$$\lg \frac{k_{ion}}{k_{ip}} = A + B \lg K_D , \qquad (14)$$

while the negative slopes suggest that the reactivity of an ion-pair decreases with increase in the interaction between its components, as had been postulated for the transition state (III). Results for the action of benzyl chloride and bromide on alkali-metal salts of methyl fluorene-9-carboxylate lie on the same graph, which indicates a parallel variation in the reactivity of ions and ion-pairs in both processes. A relation of type (14) is satisfied for certain other nucleophilic substitutions[94].

A formal kinetic interpretation of the reactivity of the anion, with the aim of explaining why it may exceed considerably that of ion-pairs in the benzylation of alkali-metal salts of 9-substituted fluorenes, but also may have the same activity ($k_{ion}/k_{ip} \approx 1$), has been based[81,82] on the scheme

$$\begin{array}{ccccc} M^+C^- + RX & \underset{k^{-1}_{ip}}{\overset{k^1_{ip}}{\rightleftarrows}} & (Complex)_1 & \xrightarrow{k^2_{ip}} & CR + MX \\ K_D \downarrow\uparrow & & & & \\ M^+ + C^- + RX & \underset{k^{-1}_{ion}}{\overset{k^1_{ion}}{\rightleftarrows}} & (Complex)_2 & \xrightarrow{k^2_{ion}} & CR + MX \end{array} \qquad (15)$$

With reversible formation of intermediate complexes, which can be termed specific solvation of one reactant by the other or e.g. coordination of the cation by the leaving group, k_{ip} and k_{ion} will actually become respectively $k^1_{ip}k^2_{ip}/(k^{-1}_{ip} + k^2_{ip})$ and $k^1_{ion}k^2_{ion}/(k^{-1}_{ion} + k^2_{ion})$. It is clear that, with operation of the mechanism (15), the ratio k_{ion}/k_{ip} will be determined by the relations between the rate constants of the individual stages; it can vary within wide limits, and be either greater or less than unity.

The influence of the medium on the reactivity of the 9-cyanofluoren-9-ide anion can be traced in its reactions with ethyl iodide[45,80,105] (Table 4) and with benzyl halides[81,82,105] (Table 5). A distinguishing feature of the first reaction is the absence of a clear effect of the dielectric constant, which is typical of nucleophilic substitution[109]. Thus the rate constant has the same value in dimethoxyethane and in hexamethylphosphoramide (ϵ = 7.2 and 30 respectively[110]); on the other hand, it decreases on passing from dimethylacetamide, dimethylformamide, and acetonitrile to ethanol (37.8, 36.7, 37.5, and 24.5[110]). This type of effect of the medium is usually interpreted in terms of the degree of solvation of the reactants and the activated complex[109].

Since the rate constant for the reaction of the 9-cyanofluoren-9-ide anion with ethyl iodide falls in parallel with the shift of the absorption band maxima of the anion to shorter wavelengths[45], it can reasonably be assumed that the factor determining the reactivity of a nucleophile is its degree of solvation. The observed sequence of variation in the solvating power of solvents

DME ≈ HMPA < DMAA < DMFA < DMSO < ethanol

characterises the solvation of the most diverse anions[109], both typically "hard" (Cl^-, N_3^-, CN^-, Br^-) and typically "soft" (SCN^-, I^-). Increase in the solvating power of dipolar aprotic solvents for these species is accompanied by decrease in the logarithm of the activity coefficients of the anions $\lg \gamma_{Y^-}$, the variation in the logarithm for each anion being almost the same in character despite the difference in absolute magnitude[109]. This enables us to compare the reactivity of the 9-cyanofluoren-9-ide anion with the logarithm for other anions (Fig. 2). In the present case we have used values of $\lg \gamma_{Y^-}$ for the thiocyanate ion, which probably resembles the 9-cyanofluoren-9-ide anion in softness, although analogous correlations exist with the logarithm for other anions. The linear dependence of

$2 + \lg k_{ion}$ on $\lg \gamma_{SCN^-}$ for four solvents (Fig. 2) is a further confirmation of the dominant role of solvation particularly of the anion. The misplacement of the point for acetonitrile is probably due to some specific effects of solvation of the activated complex.

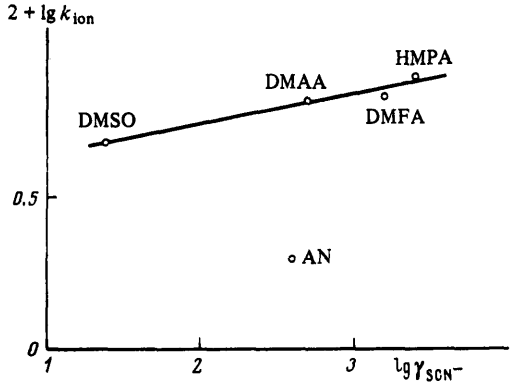


Figure 2. Correlation of reactivity of 9-cyanofluoren-9-ide anion with activity coefficients $\lg \gamma_{SCN^-}$ in a series of dipolar aprotic solvents.

The rate constant k_{ion} for the reaction with ethyl iodide decreases by a factor of 6 on passing from dimethoxyethane to ethanol (Table 4). The effect of the solvent is considerably stronger in the reactions with benzyl halides: the ratio of the rate constant in t-butyl alcohol to that in ethanol is respectively 32 and ~ 50 for benzyl chloride and bromide (Table 5). Operative factors here are probably the lower solvating power of the higher alcohol and its lower dielectric constant (11.2 and 24.5[110]). It is also possible that the activated complex is differently solvated by alcohols in the reactions of the anion with benzyl halides and with primary alkyl halides[109].

The reactivity of a carbanion (indeed of any other species) depends mainly on its stability, which may be measured by the pK_a of the original CH-acid. Apart from this, we can compare the actual rate constants of the carbanion with dissociation constants of its ion-pairs[46,52] and also with its anodic oxidation potential[111]. In reactions of anions of 9-substituted fluorenes with butyl bromide in dimethoxyethane the rate constant k_{ion} increases as the hydrocarbon becomes less acidic (Table 7), while the graph of the dependence of $\lg k_{ion}$ on pK_a is a straight line of slope 0.35.[37] The rate constant increases also with decrease in the dissociation constant of contact ion-pairs (lithium salts of 9-cyanofluorene and methyl fluorene-9-carboxylate—Table 7). In reactions with benzyl halides (Table 7), however, change in the character of the substituent at the anionic centre has hardly any effect on the reactivity of the nucleophile[81,82]. This was explained[81] in terms of the transition state, in which rupture of the carbon–halogen bond occurred to a considerably greater extent than formation of a new carbon–carbon bond. However, these deductions are in no way supported by kinetic data.

On the other hand, the increase in the rate constant for reaction of the 9-cyanofluoren-9-ide anion with benzyl chloride and bromide, on the introduction of electron-donor and electron-acceptor substituents in *meta*- and *para*-positions[105] (Table 6), presupposes synchronous rupture of the old bond and formation of the new. In this case the transition state is stabilised both by acceptors (which increase the degree of rupture of the carbon–halogen bond in comparison with the degree of formation of the carbon–carbon bond) and by donors (which increase the degree of formation of the new bond in comparison with the degree of rupture of the old bond)[105]. This transition state corresponds to a mechanism of nucleophilic substitution intermediate between S_N1 and S_N2. This would be supported by the absence of a first-order reaction with respect to the electrophilic reagent, but measurements were made[105] at only one concentration of the benzyl halide.

Reaction velocities both of free anions and of their ion-pairs are strongly dependent on the character of the leaving group and on the alkyl group. The general rules are the same for alcohols and for dimethoxyethane: $F < Cl < Br$[81,82]; $Cl < Br < I$[36,105]; $C_6H_5CH_2 \gg CH_3 > C_2H_5 >$ iso-$C_3H_7 >$ t-C_4H_9;[105] and $CH_3 > C_2H_5 > C_3H_7 > C_4H_9$.[36] Thus the rate increases as the carbon–halogen bond becomes weaker and decreases with diminution in the effective positive charge on the α carbon atom and with intensification of the steric hindrance to attack by the nucleophile due to introduction of α-alkyl groups. Variations in k_{ion}/k_{ip} in the reactions of carbanions and their ion-pairs are usually successfully interpreted[36,105] in terms of Pearson's principle[112] of hard and soft acids and bases.

2. Proton Transfer

Very great interest has been taken in proton-transfer reactions, so that many researches have been undertaken on them. We shall consider firstly studies in which the nature of the reactant species has been accurately established, and quantitative information obtained on their reactivity. We note at once that available data are largely contradictory, and the general picture is by no means clear.

Table 8. Rate constants for the reactions of polystyrylsodium and -potassium with triphenylmethane[38] at 25° C.

Cation	Solvent	k_{ion}, $M^{-1}s^{-1}$	k_{ip}, $M^{-1}s^{-1}$	$\frac{k_{ion}}{k_{ip}}$
Na^+	oxolan	178	0.15	1190
Na^+	DME	138	11	12.5
K^+	oxolan	142	<0.2	>710

Smid has investigated several proton-transfer reactions in which CH-acids act as donors, and alkali-metal salts of such acids as acceptors[17,38,113]. In the reactions of triphenylmethane with polystyrylsodium in oxolan and dimethoxyethane and with polystyrylpotassium in oxolan[38] the free anions possess the greatest reactivity, with closely similar rate constants in the two solvents (Table 8).

Since k_{ip} cannot be determined accurately, it is difficult to know how the cation influences the reactivity of the ion-pairs. On the other hand, the considerable increase in k_{ip} on passing from oxolan to dimethoxyethane suggests that solvent-separated are more active than contact ion-pairs, since the proportion of the latter is considerably higher in dimethoxyethane[43,83]. Thus the reactivity of the ionic species of "living" polystyrene towards triphenylmethane increases in the sequence from the contact to the solvent-separated ion-pair and then to the free carbanion.

Investigations on the reactions of the lithium, sodium, caesium, and tetrabutylammonium salts of fluorene with 1,2- and 3,4-benzofluorenes in oxolan, dimethoxyethane, and dioxan were more qualitative in character[17]. In almost all cases the observed rate constant increases with the concentration of the fluorenide, which would appear to prove that the free fluorenide anion is the most reactive. However, this increase is considerably larger than is to be expected for a mechanism of simultaneous involvement of ions and ion-pairs in the reaction. Thus for the reaction of fluorenyl-lithium with 3,4-benzofluorene in oxolan the constant increases by a factor of 60 when the concentration of the lithium salt is diminished by a factor of 260,[17] although at most a 16-fold increase would have been expected. In the reaction of 1,2-benzofluorene with the sodium salt of fluorene in dioxan the constant increases by a factor of 23 when the concentration of the salt decreases by a factor of 35.

The results were explained[17] on the hypothesis that ion-pairs of fluorenyl-lithium and fluorenylsodium associate, with possible formation in dioxan of aggregates of five ion-pairs, although this postulate is inconsistent with these workers' own conductivity measurements on the salts[11,15,16]. In the reaction of the caesium salt of fluorene with 1,2-benzofluorene in oxolan and dioxan the rate constant increases very moderately with dilution, which is consistent with the simultaneous participation of ions and ion-pairs in detaching the proton[17]. In this case the caesium contact ion-pair is less reactive than the fluorenide anion. A solvent-separated ion-pair may be either more or less reactive than a contact ion-pair depending on the solvent (dimethoxyethane or oxolan)[17].

There are many obscurities also in an investigation[114] on the protonation of the lithium and sodium salts of 1,3-diphenylpropene by fluorene in oxolan, 2,5-dimethyloxolan, and 2,3-dihydropyran. In oxolan the sodium salt has almost thousandfold the activity of the lithium salt. In this solvent 1,3-diphenylallyl-lithium comprises solely solvent-separated ion-pairs, whereas 1,3-diphenylallyl-sodium is a mixture of loose and intimate ion-pairs. From this it was concluded that contact ion-pairs are considerably more reactive[114]. On the other hand, in 2,5-dimethyloxolan, in which both salts are present only as contact ion-pairs, the difference in reactivity reaches a factor of almost 10^5: the rate constants at 23°C are respectively ~ 0.002 and $195\ M^{-1}\ s^{-1}$ for lithium and sodium. No allowance was made for the role of free ions (although measurements were made at concentrations of 10^{-4}–10^{-3}M) or association complexes of ion-pairs of 1,3-diphenylallyl-lithium, whose formation is very likely in this system. The exotic structure suggested[114] for the intermediate complex is frankly speculative.

In spite of some uncertainty in the reactivities of the ionic species, the results obtained by Smid[17,38,113] indicate that the rate constant for proton transfer from a CH-acid to a carbanion is independent of the difference in pK_a between the donor and the conjugate CH-acid of the carbanion. In the reaction of the polystyryl anion with triphenylmethane in oxolan we have[38] $k_{ion} \approx 150\ M^{-1}\ s^{-1}$ with $\Delta pK_a \approx 3.5$. On the abstraction of a proton by the fluorenide anion from 9-methylfluorene under the same conditions[38] $k_{ion} \approx 100\ M^{-1}\ s^{-1}$ with $\Delta pK_a \approx 0$. Less obviously the observed rate constants[38] for protonation of the dianion of 1,1-diphenylethylene by 9-propylfluorene ($\Delta pK_a \approx 10$) and of fluorenylsodium by 1,2-benzofluorene (~ 2) are approximately 20 and $10^3\ M^{-1}\ s^{-1}$ (in oxolan at 25°C).

A similar conclusion was reached by Ritchie[115], who investigated proton transfer between CH-acids and carbanions in dimethyl sulphoxide[115–118]. In this solvent alkali-metal salts of CH-acids are probably completely dissociated at low concentrations, so that the observed rate constants can be regarded as those of the free carbanions. At high concentrations of the salts, however, ionic association begins to influence the rate of proton transfer. Thus for fluorene and fluorenyl-lithium in dimethyl sulphoxide at 25°C at a salt concentration of ~ 0.5M the proton-exchange rate constant is $\sim 0.5\ M^{-1}\ s^{-1}$.[119] Yet the rate constants for proton transfer between substituted fluorenes and their carbanions at concentrations of $\sim 10^{-4}$M vary over the range 10^3–$10^4\ M^{-1}\ s^{-1}$.[116–118] It is quite possible that not only ion-pairs but also their aggregates are present at high concentrations of fluorenyl salts even in such a polar solvent as dimethyl sulphoxide.

Association plays an especially important part in the reactions of alkyl-lithium compounds. In the metallation of triphenylmethane in oxolan the reactivity of the lithium alkyls is determined not by their basicity or the acidity of the original CH-acids but by the stability of the aggregates[120,121]. With the concentration of the alkyl-lithium compound 0.1M the relative metallation rate constant increases in the sequence from methyl (1.0), vinyl (4.2), phenyl (6.3), n-butyl (23), allyl (90), to benzyl (450); the corresponding sequence at 0.01M concentration increases from methyl (1.0), phenyl (2.8), vinyl (4.3), allyl (14), n-butyl (20), to benzyl (150).

Table 9. Kinetic parameters[122,123] of the protonation of the benzyl anion and its ion-pairs in oxolan at 24°C.

Donor	Cation	$10^{-8}k_{ion}$, $M^{-1}\ s^{-1}$	$10^{-8}k_{ip}$, $M^{-1}\ s^{-1}$	$\frac{k_{ip}}{k_{ion}}$
H_2O	Na^+	0.53	55	104
MeOH	Li^+	2.3	3.4	1.5
MeOH	Na^+	2.3	58	25
MeOH	Bu_4N^+	2.3	6.0	2.6
EtOH	Na^+	1.4	37	26
EtOD	Na^+	1.2	21	17.5
t-BuOH	Li^+	0.16	9.7	61
t-BuOH	Na^+	0.16	13	81
t-BuOH	Bu_4N^+	0.16	4.6	29

The technique of pulsed radiolysis[122,123] has enabled rate constants to be determined for the very fast reactions involving protonation of the benzyl anion and its anion-pairs by various proton-donor compounds in oxolan. Benzyl anions were formed on the irradiation of solutions containing dibenzylmercury; in the presence of sodium tetraphenylborate[122] or of lithium or tetrabutylammonium perchlorate[123] their cations combine rapidly (in the case of the sodium ion the rate constant is $1.5 \times 10^{11}\ M^{-1}\ s^{-1}$) with benzyl anions to form the corresponding ion-pairs. Whether or not these salts are present the solutions contain only one ionic species, which facilitates considerably analysis of the kinetic data.

The results are quite remarkable (Table 9). Firstly, the reactivity of the ionic species increases with the acidity of the alcohol (definite rules of this type are not found in protonations involving CH-acids as donors[38,115-118]). Secondly, the rate constants for protonation of the carbanion are far smaller than the values typical of diffusion-limited processes (e.g. for detachment of a proton by the conjugate bases of NH- and OH-acids[124]). Finally, the most interesting result is that ion-pairs are considerably more active than the free carbanions. The explanation advanced[122] for this last fact was that a transition from the delocalised (benzyl) anion to an anion having a very high degree of localisation of negative charge (an oxo-anion, RO^-) takes place during the reaction. The activated complex, which will be characterised by greater charge localisation than in the original carbanion because of the involvement of an oxygen atom donating a proton, should be more stable in the presence of a cation because of the Coulombic interaction energy. From this point of view stabilisation of the activated complex by the cation would not be expected during protonation of carbanions by CH-acids, which is consistent with Smid's observations[38].

When the stability of the benzyl type of anion is enhanced, e.g. by the introduction of electron-accepting substituents into the ring, the rate constants for protonation by water and alcohols decrease[125]. Thus k_{ion} for the reaction of $C_6F_5CH_2^-$ with water and methanol in oxolan is respectively 3.3×10^6 and 1.2×10^6 M^{-1} s^{-1}. In this case, however, not only does the absolute reactivity of the carbanion decrease but the relative reactivities of the ionic species are reversed. The sodium ion-pair of the perfluorinated benzyl anion reacts at little more than one-tenth of the speed of the carbanion $k_{ip} = 4.3 \times 10^5$ M^{-1} s^{-1}. The results obtained are not yet sufficient to explain the divergence from the results for protonation of the unsubstituted benzyl anion[122,123].

The stereochemistry of protonation may provide information on the nature of the reactant species. Thus in the protonation[126] of the lithium and sodium salts of 9,10-dialkyl-9,10-dihydroanthracene in ether, oxolan, and hexamethylphosphoramide contact ion-pairs give a *cis*-product, whereas loose ion-pairs and free carbanions yield a *trans*-product.

3. Electron Transfer

Although the oxidation of carbanions is quite widely used for preparative purposes[127,128], hardly any kinetic study has been made of these processes. Quantitative information on the reactivity of ions and ion-pairs has been obtained only for oxidation of the sodium salts of 9-substituted fluorenes (with cyano, methoxycarbonyl, benzoyl, methylsulphonyl, phenylsulphonyl as substituent) by molecular oxygen in t-butyl alcohol and its mixtures with dimethyl sulphoxide[82,103,129], in which fluorenone is formed in at least 85% yield independently of the nature of the substituent. Even in this case, however, the kinetic parameters (Table 10) cannot be regarded as absolutely reliable, since corrections could not be made for salt effects due to sodium perchlorate and tetraphenylborate added§ to the reaction medium. The absence of a dependence of k_{ion} and k_{ip} on the stability of the carbanions (which may be measured by the pK_a of the original [substituted] hydrocarbon—CN 11.4,[108] $COOCH_3$ 12.9,[108] $SO_2C_6H_5$ 15.0[81]), as well as the variation of the ratio k_{ion}/k_{ip} from values exceeding unity (R = $SO_2C_6H_5$) to values less than unity (R = CN), suggests a mechanism of type (15).[82] As a consequence of the formation of an unstable intermediate product (though of unknown structure) in the oxidation of sodium methoxycarbonylfluoren-9-ide, the rate of appearance of fluorenone is only 2% of the rate of consumption of the salt[82]. The greater reactivity of the ion-pair than of the carbanion may be due[82] to involvement of the cation in stabilising the transition state (R = CN), although this may be hindered by bulky substituents at the reaction centre (R = $SO_2C_6H_5$).

§ For the determination[82,103] of reaction rate constants of ions and ion-pairs the degree of dissociation of the sodium salts was varied by adding the perchlorate and the tetraphenylborate: i.e. the calculations were based on an equation of type (11).

Table 10. Kinetic parameters[82,103] of the oxidation by molecular oxygen of the sodium salts of 9-substituted fluorenes (9-RFl^-Na^+) at 30°C.

Solvent	R	$10^4 k_{ip}$, s^{-1}	$10^4 k_{ion}$, s^{-1}	$\frac{k_{ion}}{k_{ip}}$
t-C_4H_9OH	CN	83	60	0.72
t-C_4H_9OH	COOMe	160	—	~1
t-C_4H_9OH	SO_2Ph	0.75	13	17.3
t-C_4H_9OH + 1 M DMSO	CN	3.73	0.69	0.185
t-C_4H_9OH + 1 M DMSO	SO_2Ph	0.195	1.34	6.9

The rate of oxidation of the 2-phenyldibiphenyleneallyl carbanion by molecular oxygen is greatly influenced[130] by the form in which the ion exists in solution (free or paired with an alkali-metal cation). The increase in the relative rate of oxidation in the sequence from dimethyl sulphoxide and dimethylformamide (1), pyridine (50), dimethoxyethane (~ 570), oxolan (2100), 2-methyloxolan (50 000), to diethyl and di-n-butyl ethers (> 10^5), i.e. with decrease in dielectric constant and solvating power, suggests that the most reactive species is the contact ion-pair.

In the oxidation by molecular oxygen of the triphenylmethyl anion[131,132], formed in small quantities in the presence of alkali-metal hydroxides or alkoxides, however, ion-pairs probably possess insignificant activity. In any case this provides an interpretation of the increase in the relative reaction velocity in the sequence[131] from t-butyl alcohol (< 1) through 80% pyridine–t-butyl alcohol (2), 80% dimethylformamide–t-butyl alcohol (39), 80% dimethyl sulphoxide–t-butyl alcohol (110), and 80% hexamethylphosphoramide–t-butyl alcohol (128) to hexamethylphosphoramide (> 230) or the acceleration of the process by additions of dicyclohexyl-18-crown-6.[132] Similarly, the rate of oxidation of 9-phenylfluorene, 9-methylfluorene, and 1,1-diphenylethane in the presence of potassium t-butoxide increases on passing from t-butyl alcohol to hexamethylphosphoramide[131]. It is interesting, however, that, when nitrobenzene is used as oxidant[132], the ion-pairs of the triphenylmethyl anion become more reactive than the free carbanion.

The oxidation by aromatic nitro-compounds (nitrobenzene, *m*-dinitrobenzene, *p*-nitrobenzonitrile, and 1,3,5-dichloronitrobenzene) of anions of 9-substituted fluorenes[133,134] (with methoxyl, methyl, isopropyl, amino, and

hydroxyl as substituent), formed in the presence of alkali-metal and tetra-alkylammonium methoxides in methanol, is represented by the scheme

$$\begin{gathered} RH + B^- \rightleftarrows R^- + BH, \\ R^- + PhNO_2 \rightleftarrows R^{\cdot} + PhNO_2^{\cdot-}, \\ R^{\cdot} \rightarrow {}^1/_2 R{-}R, \\ PhNO_2^{\cdot-} \rightarrow {}^2/_3 PhNO_2 + {}^1/_2 PhNO^{\cdot-}, \\ PhNO^{\cdot-} + R^{\cdot} \rightarrow \text{Nitrone}. \end{gathered} \qquad (16)$$

The complicated mechanism prevents determination of rate constants for individual stages. The rate of consumption of 9-methoxyfluorene in the presence of nitrobenzene decreases[134] in the sequence of methoxides

potassium > tetramethylammonium ≈ lithium.

4. Nucleophilic Addition

Quantitative information on the reactivity of the carbanions and their ion-pairs has been obtained for addition to a double bond[42,43,50,65,67,68,82–102,135,136] and for the cleavage of cyclic oxides of alkenes[33,137,138]. Current views on the influence of various factors on the kinetics and the mechanism of reactions involving carbanionic species are based primarily on results obtained by Szwarc and his coworkers[85–88] in an investigation of the anionic polymerisation of vinyl monomers, i.e. addition to a double bond. We shall consider only the main rules characterising these processes.

Table 11. Reaction rate constants of free ions and ion-pairs in the anionic polymerisation of alkenes at 25° C.

Anion*	Solvent	k_{ip}, $M^{-1}\,s^{-1}$					k_{ion}, $M^{-1}\,s^{-1}$	Ref.
		Li+	Na+	K+	Rb+	Cs+		
Polystyryl	cyclohexane	—	—	7.7	22.5	19	—	67
Polystyryl	benzene	—	—	47	24	18	—	65
Polystyryl	dioxan	0.9	3.4	20	21.5	24.6	—	139
Polystyryl	oxan**	19.5	17.5	30	40	—	130 000	140
Polystyryl	oxolan	160	80	~50	~50	~22	65 000	50
Polystyryl	DME	—	3600	—	—	150	40 000	83
Poly-*p*-methoxystyryl	oxolan	—	40	40	—	25	40 000	89
Poly-*o*-methylstyryl	2-methyloxolan	2	1	16	—	30	20 000	90
Poly-α-methylstyryl	dioxan	—	0.02	0.1	0.06	—	—	91
Poly-α-methylstyryl	oxan	2.6	0.047	0.25	0.26	0.26	830	91
Polyisoprenyl	oxan**	0.20	—	—	—	—	2 800	92

*The polystyryl, poly-*p*-methoxystyryl, poly-*o*-methylstyryl, poly-α-methylstyryl, and polyisoprenyl anions react respectively with styrene, *p*-methoxystyrene, *o*-methylstyrene, α-methylstyrene, and isoprene.
**Measurements made at 30° C.

Addition of an alkene molecule to an active chain-growth centre leads every time to reproduction of the centre, so that we can regard anionic polymerisation of an alkene (neglecting effects of the polymer chain, which have little significance in the formation of a carbon-chain polymer[85]) simply as a reaction of the type

$$\text{—C}^-\text{M}^+ + \text{>C=C<} \rightarrow \text{—C}^-\text{M}^+, \qquad (17)$$

where —C⁻M⁺ denotes an alkali-metal salt of a CH-acid capable of reacting either as a free ion, an ion-pair, or any other more complicated ionic species (Eqns. 1–3). Table 11 gives the most characteristic rate constants k_{ion} and k_{ip} obtained for the polymerisation of vinyl monomers (more complete information can be obtained from the above references).

The anionic polymerisation of alkenes is characterised by large differences in reactivity between free carbanions and contact ion-pairs: in solvents in which few if any solvate-separated ion-pairs are present (dioxan, oxolan, oxan, 2-methyloxolan) k_{ion} exceeds k_{ip} by factors of 10^3–10^4 (Table 11). On passing to solvents possessing a high solvating power for alkali-metal cations (dimethoxyethane, glymes), however, values of k_{ip} increase sharply[89,93], because of the higher proportion of solvent-separated ion-pairs, whose reactivity is as much as 30–50% of that of the free carbanions[42,43,83].

The presence of both loose and close ion-pairs in solution sometimes leads to an anomalous temperature variation of k_{ip}. Thus lowering the temperature from 50 to 0° C leads to an increase in k_{ip} for the reaction of polystyrylsodium with styrene in dimethoxyethane[83], and only at lower temperatures does the activation energy acquire the normal positive value. This is because the activation energy E_a determined from the Arrhenius dependence includes not only the true activation energy for the reaction of solvent-separated ion-pairs E_S but also a negative quantity ΔH_1 representing the equilibrium between ion-pairs: $E_a = E_S + \Delta H_1(1 - K_1)^{-1}$. The contribution by contact ion-pairs is insignificant, since their reactivity is only 0.1–0.01% of that of solvent-separated ion-pairs, and can be neglected[83]. The activation energy E_a can be either positive or negative depending on the absolute values of E_S and ΔH_1, as well as the value of K_1 at the given temperature.

If the solvent is unable to separate the ion-pairs, the Arrhenius graph will be linear[83,43,95]. The measured k_{ip} constants then represent the reactivity only of contact ion-pairs. For the polymerisation of styrene in dioxan k_{ip} increases[139] in the sequence

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+,$$

since increase in the size of the alkali-metal cation facilitates separation of the ionic fragments in the transition state; in this case $\lg k_{ip}$ is a linear function of $(r_{M^+} + 2)^{-1}$, where r_{M^+} is the radius of the cation. On polymerisation of the same monomer in cyclohexane and benzene, in which ion-pairs are definitely of the contact type[65,67], or of α-methylstyrene in dioxan[91], no definite tendency for k_{ip} to vary with the cationic radius is observed, which suggests that other factors are operating, besides the energy of electrostatic interaction between carbanion and gegenion.

It is noteworthy that the characteristics of the solvent—its dielectric constant and solvating power—do not in fact affect the reactivity of contact ion-pairs (Table 11). Rubidium and caesium ion-pairs react at almost the same rate in the polymerisation of styrene in cyclohexane, benzene, dioxan, oxan, and oxolan. Only with the sodium and lithium salts does k_{ip} increase in the sequence dioxan < oxan < oxolan, but this is now due to the participation of solvent-separated ion-pairs in the reaction. It may therefore be assumed that chain growth, like many other bimolecular reactions, involves formation of an intermediate complex, whose conversion into the product is the limiting stage. A similar complex is probably formed

also in the reaction between the alkene and the free carbanion. In any case, k_{ion} also does not depend explicitly on the nature of the solvent[96]: in hexamethylphosphoramide, dimethoxyethane, oxolan, oxan, 2-methyloxolan, mixtures of oxolan with dioxan and with benzene, and oxepan it has the respective values 92 000,[42] 40 000,[83] 65 000,[50] 130 000,[140] 30 000,[97] 60 000,[98] 40 000–70 000,[99] and 100 000 [100] M^{-1} s^{-1}. We can compare, for example, hexamethylphosphoramide and oxepan: in these solvents the polystyryl anion has almost the same reactivity (k_{ion} = 92 000 [42] and 100 000 [100] M^{-1} s^{-1}), although the dielectric constants—30 [110] and 5.06 [100]—differ sixfold. Solvation of the carbanion would obviously play an insignificant part, although it has been adduced[89,90] to explain the effect of an electric field on the rate of the anionic polymerisation of substituted styrenes.

Studies have appeared recently[68,69,136] on the anionic polymerisation of vinyl monomers in the presence of cations of bivalent metals, but analysis of the kinetic data is made difficult by the formation of association complexes and the two-stage mechanism of the dissociation of alkaline-earth metal salts.

The polymerisation of 2-vinylquinoline [101] and of 2-, 3-, and 4-vinylpyridines [102,135] yields polymers capable of solvating the alkali-metal cation of an ion-pair to a greater extent than the monomers. Furthermore, the nitrogen atom of the pyridyl group is involved in delocalisation of the negative charge[135]: i.e. the growing anion is ambident. The combination of these effects leads to rules characterising the reactivity and the electrical conductivity of alkali-metal salts of these "living" polymers that differ from those observed for such salts of the polystyryl anion.

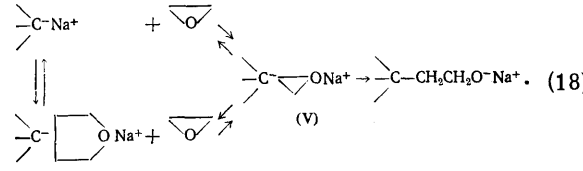
Table 12. Kinetic parameters[82] of the reactions of sodium salts of 9-substituted fluorenes (9-RFl$^-$Na$^+$) with acrylic esters in t-butyl alcohol at 30° C.

Methyl ester	R	$10^3 k_{ip}$, M^{-1} s^{-1}	$10^3 k_{ion}$, M^{-1} s^{-1}	$\frac{k_{ion}}{k_{ip}}$
Acrylate	CN	760	760	1
Acrylate	COOMe	1700	1700	1
Acrylate	SO_2Ph	1600	1600	1
Methacrylate	CN	8.6	8.6	1
Methacrylate	COOMe	10	400	40
Methacrylate	SO_2Ph	34	2200	65
Crotonate	CN	5.2	5.2	1
Crotonate	COOMe	7.6	70	9
Crotonate	SO_2Ph	6.7	690	103

Whereas free carbanions are far more active than contact ion-pairs in the polymerisation of vinyl monomers, these species have in most cases the same reactivity in the reactions of the sodium salts of 9-substituted fluorenes (9-RFl$^-$Na$^+$) with methyl acrylate, methacrylate, and protonate in t-butyl alcohol[82] (Table 12). Formation of the Michael product is assumed to have a mechanism of type (15). The variation of the reactivity of the acrylic esters is due both to polar factors and to steric factors (e.g. resulting from introduction of a methyl group).

The formation of intermediate complexes of carbanions and their ion-pairs with electrophiles, leading to a mechanism of type (15), is assumed in nucleophilic substitutions[82], in nucleophilic additions[52,137,138], and in electron-transfer processes[82]. However, it is by no means always possible to detect them: usually only kinetic evidence is available.

Such a complex can be detected spectroscopically in the reaction of sodium 9-methylfluoren-9-ide with oxiran[137] in oxan and oxolan at −30° C. The intermediate complex (V) is actually formed by separation of a contact ion-pair by a reactant molecule or by displacement of a solvent molecule from a solvent-separated ion-pair:



(18)

The presence in the epoxide molecule of two centres—electrophilic (a carbon atom) and nucleophilic (the oxygen atom)—makes a push–pull mechanism possible in this reaction[52,137,138], which may be so efficient that the reactivity of the contact type of ion-pair will exceed considerably that of the free carbanion[52,138]. Such is the situation e.g. in the cleavage of the epoxide ring of fluoradenylsodium in oxiran solution[138]. The observed rate constant increases with the concentration of the salt and with the introduction of excess of sodium tetraphenylborate. On the other hand, on the addition of solvating additives—crown polyethers and cryptate (diazahexaoxobicyclic polyether [$N(CH_2CH_2[OCH_2CH_2]_2)_3N$])—the rate constant drops sharply. Reaction of the lithium salt of fluoradene is characterised by similar rules. However, the caesium salt is extremely unreactive, perhaps because the large caesium cation is only slightly electrophilic.

Table 13. Kinetic parameters[52] of the reactions of alkali-metal salts of carbanions with oxiran in oxolan at 25° C.

Anion	Cation	k_{ip}, M^{-1} s^{-1}	k_{ion}, M^{-1} s^{-1}	$\frac{k_{ion}}{k_{ip}}$
Polytolanyl	Na^+	0.065	1.1	17
Polystyryl	Li^+	$7.2 \cdot 10^3$		0.03
Polystyryl	Na^+	13.8		13
Polystyryl	K^+	6.0	~200	33
Polystyryl	Rb^+	3.4		57
Polystyryl	Cs^+	1.7		122
Poly-α-methylstyryl	Na^+	120	2900	24

The importance of the size of the alkali-metal cation for a push–pull mechanism of ring cleavage in oxiran follows also from the data[52] in Table 13. Although the increase in k_{ip} with decrease in cationic size from caesium to sodium in the salts of the polystyryl anion might indicate formally an increase in the contribution by solvent-separated ion-pairs, the sharp drop in k_{ip} on passing to the lithium salt ($k_{ion}/k_{ip} \approx 0.3$) can result only from electrophilic collaboration of the lithium cation. The difference in relative reactivities of the carbanions on reaction with the epoxide and with the alkene also suggests that the cation plays an important part in the transition state: in the former case k_{ion}/k_{ip} varies between 10 and 100 (Table 13), but in the latter between 1000 and 10 000 (Table 11).

The reactivities of the polystyryl, polytolanyl, and poly-α-methylstyryl anions towards oxiran may be measured by the dissociation constants of their sodium salts[52]: k_{ion} is greater the smaller is K_D, and the dependence of

$\lg k_{ion}$ on $\lg K_D$ is linear. Thus the dissociation constant reflects the stability of these species, as in the case of the anions of 9-substituted fluorenes.

REFERENCES

1. H.Sadek and R.M.Fuoss, J.Amer.Chem.Soc., 76, 5897, 5905 (1954).
2. L.D.McKeever, in "Ions and Ion Pairs in Organic Reactions" Edited by M.Szwarc (Translated into Russian), Mir, Moscow, 1975, p.292.
3. A.L.Kurts, I.P.Beletskaya, and O.A.Reutov, Vestnik Moskov.Univ., Khim., 387 (1974).
4. N.Kornblum, P.J.Berrigan, and W.J.Le Noble, J.Amer.Chem.Soc., 85, 1141 (1963).
5. H.O.House, "Modern Synthetic Reactions", Menlo Park, Cal., 1972, Ch.9.
6. I.Forsblad, Arkiv Kemi, 15, 403 (1960).
7. A.I.Shatenshtein, "Izotopnyi Obmen i Zameshchenie Vodoroda v Organicheskikh Soedineniyakh" (Isotope Exchange and Hydrogen Substitution in Organic Compounds), Izd.Akad.Nauk SSSR, Moscow, 1960.
8. C.D.Ritchie, in "Solute-Solvent Interactions", Marcel Dekker, New York, 1969.
9. A.Streitwieser, D.E.Van Sickle, and W.C.Langworthy, J.Amer.Chem.Soc., 84, 244 (1962).
10. A.Streitwieser and J.Hammons, Progr.Phys.Org.Chem., 3, 41 (1965).
11. T.E.Hogen-Esch and J.Smid, J.Amer.Chem.Soc., 88, 307 (1966).
12. L.L.Chan and J.Smid, J.Amer.Chem.Soc., 90, 4654 (1968).
13. T.E.Hogen-Esch and J.Smid, J.Amer.Chem.Soc., 91, 4580 (1969).
14. T.E.Hogen-Esch and J.Smid, J.Phys.Chem., 79, 233 (1975).
15. T.E.Hogen-Esch and J.Smid, J.Amer.Chem.Soc., 87, 669 (1965).
16. T.E.Hogen-Esch and J.Smid, J.Amer.Chem.Soc., 88, 318 (1966).
17. L.L.Chan and J.Smid, J.Amer.Chem.Soc., 89, 2764 (1967).
18. L.L.Chan, K.H.Wong, and J.Smid, J.Amer.Chem.Soc., 92, 1955 (1970).
19. U.Takaki, T.E.Hoden-Esch, and J.Smid, J.Amer.Chem.Soc., 93, 6760 (1971).
20. K.H.Wong, G.Konizer, and J.Smid, J.Amer.Chem.Soc., 92, 666 (1970).
21. T.Ellingsen and J.Smid, J.Phys.Chem., 73, 2712 (1969).
22. J.Smid, Angew.Chem.Internat.Ed., 11, 112 (1972).
23. U.Takaki, T.E.Hogen-Esch, and J.Smid, J.Phys.Chem., 76, 2152 (1972).
24. G.L.Collins and J.Smid, J.Amer.Chem.Soc., 95, 1503 (1973).
25. G.C.Greenacre and R.N.Young, J.Chem.Soc., Perkin Trans.II, 1661 (1975).
26. J.W.Burley and R.N.Young, J.Chem.Soc.(B), 1018 (1971).
27. J.W.Burley and R.N.Young, J.Chem.Soc., Perkin Trans.II, 1006 (1972).
28. J.W.Burley and R.N.Young, J.Chem.Soc., Perkin Trans.II, 835 (1972).
29. R.Waak, M.A.Doran, and P.E.Stevenson, J.Amer.Chem.Soc., 88, 2109 (1966).
30. J.B.Grutzner, J.M.Lawlor, and L.M.Jackman, J.Amer.Chem.Soc., 94, 2306 (1972).
31. F.J.Kronzer and V.R.Sandel, J.Amer.Chem.Soc., 94, 5750 (1972).
32. D.Casson and B.J.Tabner, J.Chem.Soc.(B), 572 (1969).
33. E.de Boer and J.L.Sommerdijk, see Ref.2, p.318.
34. K.S.Chen and N.Hirota, in "Methods for the Investigation of Fast Reactions" (Translated into Russian), Mir, Moscow, 1977, p.627.
35. J.Smid, see Ref.2, p.98.
36. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Zhur.Org.Khim., 12, 2287 (1976).
37. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Zhur.Org.Khim., 12, 2489 (1976).
38. L.L.Chan and J.Smid, J.Phys.Chem., 76, 695 (1972).
39. C.J.Pedersen and H.K.Frensdorff, Angew.Chem.Internat.Edn., 11, 16 (1972).
40. J.M.Lehn, Structure and Bonding, 16, 1 (1974).
41. E.Swift, J.Amer.Chem.Soc., 60, 1403 (1938).
42. L.L.Böhm and G.V.Shulz, European Polymer J., 11, 265 (1975).
43. T.Shimomura, K.J.Tölle, J.Smid, and M.Szwarc, J.Amer.Chem.Soc., 89, 796 (1967).
44. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Zhur.Org.Khim., 12, 725 (1976).
45. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Dokl.Akad.Nauk SSSR, 232, 343 (1977).
46. A.Kh.Bagdasar'yan, B.A.Dolgoplosk, and V.M.Frolov, Dokl.Akad.Nauk SSSR, 198, 1077 (1971).
47. J.T.Denison and J.B.Ramsey, J.Amer.Chem.Soc., 77, 7615 (1955).
48. Y.H.Inami, H.K.Bodenson, and J.B.Ramsey, J.Amer.Chem.Soc., 83, 4745 (1961).
49. C.Carvajal, K.J.Tölle, J.Smid, and M.Szwarc, J.Amer.Chem.Soc., 87, 5548 (1965).
50. D.N.Bhattacharyya, C.L.Lee, J.Smid, and M.Szwarc, J.Phys.Chem., 69, 612 (1965).
51. M.Van Beylen, D.N.Bhattacharyya, J.Smid, and M.Szwarc, J.Phys.Chem., 70, 157 (1966).
52. A.A.Solov'yanov and K.S.Kazanskii, Vysokomol.Soed., A16, 595 (1974).
53. D.J.Cram, "Fundamentals of Carbanion Chemistry" (Translated into Russian), Mir, Moscow, 1967.
54. R.M.Fuoss and C.A.Kraus, J.Amer.Chem.Soc., 55, 1019, 2387 (1933).
55. L.D.Pettit and S.Bruckenstein, J.Amer.Chem.Soc., 88, 4783 (1966).
56. M.Morton, E.E.Bostick, and R.Livigni, Rubber Plastics Age, 42, 397 (1961).
57. D.J.Worsfold and S.Bywater, Canad.J.Chem., 38, 1891 (1960).
58. M.Morton, L.J.Fetters, and E.E.Bostick, J.Polymer Sci., C, 1, 311 (1963).
59. A.F.Johnson and D.J.Worsfold, J.Polymer Sci., A, 3, 449 (1965).
60. Yu.A.Spirin, A.R.Gantmakher, and S.S.Medvedev, Dokl.Akad.Nauk SSSR, 146, 368 (1962).
61. H.Sinn and F.Patat, Angew.Chem., 75, 805 (1963).
62. D.J.Worsfold and S.Bywater, Canad.J.Chem., 42, 2884 (1964).
63. D.K.Polyakov, A.R.Gantmakher, and S.S.Medvedev, Vysokomol.Soed., 7, 182 (1965).

64. R.V.Basova, A.R.Gantmakher, and S.S.Medvedev, Dokl.Akad.Nauk SSSR, 169, 368 (1966).
65. J.E.L.Roovers and S.Bywater, Trans.Faraday Soc., 62, 701 (1966).
66. S.Bywater and D.J.Worsfold, Canad.J.Chem., 40, 1564 (1962).
67. J.E.L.Roovers and S.Bywater, Canad.J.Chem., 46, 2711 (1968).
68. C.Mathis, L.Christmann-Lamande, and B.François, Makromol.Chem., 176, 931 (1975).
69. B.I.Nakhmanovich, R.V.Basova, and A.A.Arest-Yakubovich, J.Macromol.Sci., A, 9, 575 (1975).
70. M.Weiner, G.Vogel, and R.West, Inorg.Chem., 1, 654 (1962).
71. T.L.Brown, D.W.Dickerhoof, and D.A.Bafus, J.Amer.Chem.Soc., 84, 1371 (1962).
72. E.Weiss and E.A.C.Lucken, J.Organometallic Chem., 2, 197 (1964).
73. T.L.Brown and M.T.Rogers, J.Amer.Chem.Soc., 79, 1859 (1957).
74. G.Wittig and F.J.Meyer, Annalen, 571, 167 (1951).
75. D.Margerison and J.P.Newpont, Trans.Faraday Soc., 59, 2058 (1963).
76. D.Margerison and J.D.Pont, Trans.Faraday Soc., 67, 353 (1971).
77. S.F.Acree, Amer.Chem.J., 48, 352 (1912).
78. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Izd.Akad.Nauk SSSR, Ser.Khim., 1678 (1975).
79. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Izd.Akad.Nauk SSSR, Ser.Khim., 2363 (1975).
80. A.A.Solov'yanov, P.I.Dem'yanov, I.P.Beletskaya, and O.A.Reutov, Zhur.Org.Khim., 12, 718 (1976).
81. D.Bethell, C.S.Fairclough, and R.G.Wilkinson, J.Chem.Soc., Perkin Trans.II, 1090 (1975).
82. D.Bethell, C.S.Fairclough, and R.J.E.Talbot, J.Chem.Soc., Perkin Trans.II, 55 (1976).
83. T.Shimomura, J.Smid, and M.Szwarc, J.Amer.Chem.Soc., 89, 5743 (1967).
84. M.Shinohara, J.Smid, and M.Szwarc, Chem.Comm., 1232 (1969).
85. M.Szwarc, "Anionic Polymerisation" (Translated into Russian), Mir, Moscow, 1971.
86. M.Szwarc, in "Ions and Ion Pairs in Organic Reactions", Wiley-Interscience, New York, 1974, Vol.2.
87. M.Szwarc, Science, 170, 23 (1970).
88. M.Szwarc, Accounts Chem.Res., 2, 87 (1969).
89. K.Takaya, H.Hirohara, M.Nakayama, and N.Ise, Trans.Faraday Soc., 67, 119 (1971).
90. H.Hirohara, M Nakayama, R.Kawabata, and N.Ise, Trans.Faraday Soc., 68, 51 (1972).
91. F.S.Dainton, G.A.Harpell, and K.J.Ivin, European Polymer J., 5, 395 (1969).
92. S.Bywater and D.J.Worsfold, Canad.J.Chem., 45, 1821 (1967).
93. M.Shinohara, J.Smid, and M.Szwarc, J.Amer.Chem.Soc., 90, 2175 (1968).
94. J.E.Gordon, "The Organic Chemistry of Electrolyte Solutions", Wiley-Interscience, New York, 1975, p.468.
95. C.Stretch and G.Allen, Polymer, 2, 151 (1961).
96. B.Schmitt and G.V.Schulz, European Polymer J., 11, 119 (1975).
97. M.Van Beylen, M.Fisher, J.Smid, and M.Szwarc, Macromolecules, 2, 575 (1969).
98. R.H.Schuler and W.H.Hamill, J.Amer.Chem.Soc., 74, 6171 (1952).
99. W.Van Dusen and W.H.Hamill, J.Amer.Chem.Soc., 84, 3648 (1962).
100. G.Löhr and S.Bywater, Canad.J.Chem., 48, 2031 (1970).
101. A.Rigo, M.Szwarc, and G.Sackmann, Macromolecules, 4, 622 (1971).
102. M.Tardi and P.Sigwalt, European Polymer J., 8, 151 (1972); 9, 1369 (1973).
103. D.Bethell, R.J.E.Talbot, and R.G.Wilkinson, Chem.Comm., 1528 (1968).
104. A.A.Solov'yanov and K.S.Kazanskii, Vysokomol.Soed., A14, 1063 (1972).
105. K.Bowden and R.S.Cook, J.Chem.Soc.(B), 1529 (1968).
106. C.D.Ritchie and R.E.Uschold, J.Amer.Chem.Soc., 90, 2821 (1968).
107. N.K.Genkina, A.L.Kurts, I.P.Beletskaya, and O.A.Reutov, Dokl.Akad.Nauk SSSR, 189, 1252 (1969).
108. K.Bowden and R.Stewart, Tetrahedron, 21, 261 (1965).
109. R.Alexander, E.C.F.Ko, A.J.Parker, and T.J.Broxton, J.Amer.Chem.Soc., 90, 5049 (1968).
110. J.A.Riddick and W.B.Bunger, "Organic Solvents", Wiley-Interscience, New York, 1970.
111. P.Lochert and P.Federlin, Tetrahedron Letters, 1109 (1973).
112. R.G.Pearson and J.Songstad, J.Amer.Chem.Soc., 89, 1827 (1967).
113. K.H.Wong, G.Konizer, and J.Smid, J.Amer.Chem.Soc., 92, 666 (1970).
114. G.C.Greenacre and R.N.Young, J.Chem.Soc., Perkin Trans.II, 1636 (1976).
115. C.D.Ritchie and R.E.Uschold, J.Amer.Chem.Soc., 89, 2960 (1967).
116. C.D.Ritchie and R.E.Uschold, J.Amer.Chem.Soc., 90, 3415 (1968).
117. C.D.Ritchie and R.E.Uschold, J.Amer.Chem.Soc., 89, 1730 (1967).
118. C.D.Ritchie, J.Amer.Chem.Soc., 91, 6749 (1969).
119. J.I.Brauman, D.F.McMillen, and Y.Kanazawa, J.Amer.Chem.Soc., 89, 1728 (1968) [sic].
120. R.Waack and P.West, J.Amer.Chem.Soc., 86, 4494 (1964).
121. P.West and R.Waack, J.Amer.Chem.Soc., 92, 840 (1970).
122. B.Bockrath and L.M.Dorfman, J.Amer.Chem.Soc., 96, 5708 (1974).
123. B.Bockrath and L.M.Dorfman, J.Amer.Chem.Soc., 97, 3307 (1975).
124. M.Eigen, in "Prix Nobel 1967", Stockholm, 1969.
125. A.K.Pikaev, G.A.Artamkina, and I.P.Beletskaya, Dokl.Akad.Nauk SSSR, 232, 634 (1967).
126. E.J.Panel and T.J.Rodgers, J.Amer.Chem.Soc., 96, 6921 (1974).
127. G.A.Russel, E.G.Janzen, A.G.Bemis, E.J.Ceels, A.J.Moye, S.Mak, and E.T.Strom, Advances in Chemistry Series, 51, 112 (1965).
128. G.A.Russel, A.G.Bemis, E.J.Geels, E.G.Janzen, and A.J.Moye, Advances in Chemistry Series, 75, 174 (1968).
129. D.Bethell and R.J.E.Talbot, J.Chem.Soc.(B), 638 (1968).
130. J.G.Pacifici, J.E.Garst, and E.G.Janzen, J.Amer.Chem.Soc., 87, 3014 (1965).

131. G.A.Russel and A.G.Bemis, J.Amer.Chem.Soc., 88, 5491 (1966).
132. R.D.Guthrie, G.R.Weisman, and L.G.Burdon, J.Amer.Chem.Soc., 96, 6955 (1974).
133. R.D.Guthrie, D.P.Wesley, G.W.Pendygraft, and A.T.Young, J.Amer.Chem.Soc., 98, 5870 (1976).
134. R.D.Guthrie, G.W.Pendygraft, and A.T.Young, J.Amer.Chem.Soc., 98, 5877 (1976).
135. C.J.Chang, R.F.Kiesel, and T.E.Hogen-Esch, J.Amer.Chem.Soc., 97, 2805 (1975).
136. B.I.Nakhimovich, V.A.Korolev, and A.A.Arest-Yakubovich, Vysokomol.Soed., A18, 1480 (1976).
137. P.Sigwalt, "Twenty-third International Congress of Pure and Applied Chemistry, Boston, U.S.A., 1971", Special Lectures, Vol.4, p.495.
138. C.J.Chang, R.F.Kiesel, and T.E.Hogen-Esch, J.Amer.Chem.Soc., 95, 8446 (1973).
139. D.N.Bhattacharyya, J.Smid, and M.Szwarc, J.Phys.Chem., 69, 624 (1965).
140. A.Parry, J.E.L.Roovers, and S.Bywater, Macromolecules, 3, 355 (1970).

Department of Organic Chemistry,
Faculty of Chemistry,
Moscow State University