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**Review**

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# THE ROLE OF ION PAIRS IN $S_E$ REACTIONS OF ORGANOMETALLIC COMPOUNDS

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## Introduction

Of the four possible mechanisms for heterolytic substitution at a saturated carbon, three were known at the start of the sixties: $S_N2$, $S_N1$, and $S_E2$ *. The last possible mechanism, the monomolecular $S_E1$ mechanism was discovered in 1962 [5,6]. A characteristic of $S_E1$ reactions is the fact that in the rate-determining step of the process, the substrate is attacked by some nucleophilic reagent, present in solution, while reaction with an electrophilic reagent occurs in the fast step. If a suitable nucleophilic catalyst (N) is lacking in the system, then, as a rule, the reaction does not take place or else is accomplished by the $S_E2$ mechanism (under the condition that the nucleophilicity of the R radical and the electrophilicity of the attacking reagent are fairly high). Consequently, the monomolecular electrophilic substitution processes should be classified as $S_E1(N)$ reactions. It is postulated that attack by the nucleophile causes ionization of the C–M bond, and that then the equilibrium is quickly shifted under the influence of the electrophilic reagent:

$$\mathrm{R{-}M + N} \underset{k_{-1}}{\overset{k_1(\text{slow})}{\rightleftharpoons}} \left[\mathrm{R^{\delta-}{-}^{\delta+}M{-}N}\right] \rightleftarrows \underset{\text{ion pair}}{\mathrm{R^-MN^+}} \xrightarrow[\text{E–N}]{k_2(\text{fast})} \mathrm{RE + MN}$$

(rate $= k_1$ [RM][N], if $k_2 \gg k_{-1}$).

Either anions or neutral molecules (for example, solvent molecules that are capable of coordinating to the metal atoms in R–M) are capable of fulfilling the role of the nucleophile N. Finally, reactions are possible in which the nucleophilic portion of the electrophilic agent E–N can function as the nucleophilic catalyst. In this case it is especially difficult to choose between the $S_E1$ and $S_E2$ ($S_Ei$) mechanisms, since the observed formal kinetic order should be equal to two **.

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* See refs. 1–4 for reviews on the $S_E2$ mechanism.

** As the criterion of assigning substitution reactions to the monomolecular type $S_E1$ (as well as $S_N1$), independent of the formal kinetic order, it is assumed that one covalent change (cleavage of the covalent bond) occurs in the slow step of the reaction.

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The $S_E1$ mechanism was first discovered for the example of the isotopic exchange of the ethyl ester of $\alpha$-bromomercuriphenylacetic acid with $^{203}HgBr_2$ in DMSO [5,6]:

$$C_6H_5CH(HgBr)COOEt + \overset{\bullet}{Hg}Br_2 \overset{DMSO}{\rightleftarrows} C_6H_5CH(\overset{\bullet}{Hg}Br)COOEt + HgBr_2$$

The reaction is first order in the organomercury compound and zero order in mercuric bromide. Ionization of the organomercury compound occurs in the first step, which is facilitated by aprotic bipolar solvents (for example, DMSO), while in the second step the ion pair formed quickly reacts with the electrophile ($\overset{\bullet}{Hg}Br_2$). The degree of ionization in the transition state should depend on the strength of the nucleophile and on the stability of the carbanion entering into the composition of the ion pair. The fairly stable carbanion of phenylacetic ester ($pK_a$ 17) quickly assumes a planar configuration, as a result of which racemization occurs [7].

Later, other reactions following a $S_E1(N)$ mechanism were discovered: isotopic exchange of $p$-nitrobenzylmercury bromide with $\overset{\bullet}{Hg}Br_2$ in DMSO [8], protolysis of $R_2Hg$ by HCl in dimethylformamide [9], decomposition of $\alpha$-(4-pyridinium)methylmercury chloride with dilute aqueous $HClO_4$, catalyzed by chloride ions [10–12], protolysis of 2-chloromercury-1,3-dimethylbenzylimidazol ion, catalyzed by chloride ions [13], reactions of proto- and iodo-demercuration of $\beta$-chlorovinylmercury chlorides [14–16], isotopic exchange of pentafluorophenylmercury bromide with $\overset{\bullet}{Hg}Br_2$ in DMSO [17].

The concepts concerning the $S_E1(N)$ mechanism can be applied successfully to explain a number of $S_E$ reactions which previously seemed incomprehensible [18–25]. Starting with the idea discussed of the nature of $S_E1(N)$ reactions, the protolysis of some organomercury compounds by water in DMF solution was accomplished in the presence of $I^-$ as the catalyst [26] *. A number of organomercurials which

$$R_2Hg + 2H_2O + 2I^- \rightarrow 2RH + HgI_2 + 2OH^-$$

exhibit low reactivity under conditions favoring the $S_E2$ mechanism, were selected as models (R = CClFCOOEt, $C_6F_5$, $CF_3$). The rate of the reactions was studied polarographically **. The reaction rate is strongly dependent on the nature of the R radical (for example, $k \times 10^6$, $s^{-1}$ for R = $CF_3$ is equal to 0.3, and is 295 for R = CFClCOOEt). The reactions were run under pseudo-monomolecular conditions (in the presence of excess water); due to this it was impossible to apply kinetic criteria in order to establish the mechanism. A distinct linear relationship between log $k$ and the $pK_a$ of the corresponding RH hydrocarbons suggests classification of this protolysis reaction to the $S_E1(N)$ mechanism ***.

### The role of ion pairs and the new mechanism of $S_E$ reactions: the ion-pair mechanism ($S_E2$i.p.)

When studying halo- and mercuri-destannation reaction [31–34] it was established that, in accord with the $S_E2$ mechanism, the rate of the reactions decreases

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* Reversal of this $S_E1(N)$ reaction was realized by G.B. Deacon [27].

** The reaction does not take place in the absence of $I^-$, nor in anhydrous DMF solution containing $Bu_4NI$.

*** The publication [28] in which doubt was cast on the $S_E1(N)$ mechanism of the discussed reaction, and where instead an oxidative mechanism was proposed, was based on a fallacious experiment, as was established when the study was repeated [29,30].

when going from $C_6H_5Sn(CH_3)_3$ to $C_6F_5Sn(CH_3)_3$, but for the organotin compounds containing stronger electron-accepting groups ($R = C_6H_5C{\equiv}C$, 9-fluoranyl, indenyl, etc.), the reaction rate increases sharply, although the reaction continues to follow second order kinetics [32–35].

*Mercuridestannation*

$$RSnMe_3 + HgCl_2 \xrightarrow[DMSO]{k_2} RHgCl + Me_3SnCl$$

| R | $\underbrace{CN, \text{cyclo-}C_5H_5, C_6H_5C{\equiv}C, CH_2{=}CHCH_2}$ $\gg$ | $CH_2{=}CH >$ |
|---|---|---|
| $k_2^{25}(l\ mol^{-1}\ s^{-1})$ | Very fast | 112 |

| R | $> C_6H_5$ | $> CH_3$ | $> C_6F_5$ |
|---|---|---|---|
| $k_2^{25}(l\ mol^{-1}\ s^{-1})$ | 50 | 5.0 | 0.96 |

*Halodestannation*

$$RSnMe_3 + I_2 \xrightarrow[DMSO]{k_2} RI + Me_3SnI$$

| R | $CH_2{=}CHCH_2 >$ | $C_9H_7 >$ | $C_6H_5C{\equiv}C \gg$ | $CH_2{=}CH \approx$ |
|---|---|---|---|---|
| $k_2^{25}(l\ mol^{-1}\ s^{-1})$ | $2.3 \times 10^7$ | $9.5 \times 10^6$ | $3.4 \times 10^6$ | 63 |

| R | $\approx C_6H_5$ | $\approx CH_3$ | $\approx C_6F_5$ |
|---|---|---|---|
| $k_2^{25}(l\ mol^{-1}\ s^{-1})$ | 42 | 53 | 57 |

$$RSnMe_3 + Br_2 \xrightarrow[DMF/CCl_4]{k_2} RBr + Me_3SnBr$$

| R | $C_9H_7$ | $\gg 9\text{-}CH_3C_{13}H_8 >$ | $C_6H_5$ |
|---|---|---|---|
| $k_2^{25}(l\ mol^{-1}\ s^{-1})$ | $1.2 \times 10^8$ | $4.1 \times 10^4$ | $1.35 \times 10^4$ |

The halogenation of $RSnMe_3$ ($R = \text{cyclo-}C_5H_5$, $CH_3COCH_2$, CN) in DMSO proceeded by a first order mechanism (zero order in electrophilic agent), i.e., the $S_E1$ mechanism was realized in this case [35].

$$RSnMe_3 + I_2 \xrightarrow[DMSO]{k_1} RI + Me_3SnI$$

| R | CN | $CH_3COCH_2$ | $\text{cyclo-}C_5H_5$ |
|---|---|---|---|
| $k_1^{20}(s^{-1})$ | 0.33 | 0.25 | 4.1 |

Many of the reactions mentioned were accomplished so rapidly that they could be studied only by the jet technique.

A similar increase in the rate of a process with increase in the electronegativity of the group R was observed in the reaction of $RSnMe_3$ with iodine in $CCl_4$ or DMSO. Note that in all of the reactions discussed only the R–Sn * (or R–Ge [36]) bond was

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* A special case is apparently represented by $CH_2{=}CHCH_2SnMe_3$, which reacts with an "anomalously" fast rate with mercuric chloride and halogens. This is probably related to the possibility of either the $S_Ei$ or $S_E2$ mechanisms for attack "in the tail" of the molecule, where steric hindrance decreases substantially and as a result of which the reaction should proceed with allylic rearrangement.

cleaved and, depending on the nature of R, the reaction was either second or first order in electrophilic agent.

$$RSnMe_3 + I_2 \xrightarrow{CCl_4} RI + Me_3SnI$$

| R | $CH_2{=}CHCH_2 \gg$ | $C_6H_5C{\equiv}C >$ | $C_6H_5$ | $> CH_2{=}CH >$ |
|---|---|---|---|---|
| $k_3^{20}$ (l mol$^{-1}$ s$^{-1}$) | $1.9 \times 10^6$ | $1.8 \times 10^3$ | $2.3 \times 10^2$ | 31.2 |

| | $> C_6H_5CH_2 >$ | $C_6H_5 \gg$ | $CH_3$ |
|---|---|---|---|
| | 27.8 | 15.0 | very slow |

| R | $CN >$ | cyclo-$C_5H_5 >$ | $C_9H_7$ |
|---|---|---|---|
| $k_2^{20}$(l mol$^{-1}$ s$^{-1}$) | $2.3 \times 10^3$ | $5.0 \times 10^2$ | $1.6 \times 10^2$ |

$$RGeMe_3 + I_2 \xrightarrow{DMSO} RI + Me_3GeI$$

| R | $m$-$CH_3C_6H_4 >$ | $CH_3$ | $>$ cyclo-$C_5H_5 >$ |
|---|---|---|---|
| $k_3^{25}$(l mol$^{-1}$ s$^{-1}$) | $8.5 \times 10^{-3}$ | $1.9 \times 10^{-6}$ | $2.5 \times 10^3$ |

| | $> C_9H_7 >$ | $9\text{-}CH_3C_{13}H_8$ |
|---|---|---|
| | 67 | $1.2 \times 10^{-4}$ |

The second order kinetics in iodine observed in these reactions demonstrates the involvement of two iodine molecules in these cases, one of which functions as the catalyst.

A similar picture is observed when organomercury compounds are treated with mercuric chloride in DMF. In view of the fact that the reaction rate decreases with increasing electronegativity of the R group (decreases in the p$K_a$ of RH), it may be assumed that a mechanism of the $S_E2$ type is realized in this case:

$$R_2Hg + HgCl_2 \xrightarrow[DMF]{k_2} 2RHgCl$$

| R | $\underbrace{C_6H_5, \quad CH_2{=}CH}$ | | $\gg C_2H_5 >$ | $C_6H_5CH_2 >$ |
|---|---|---|---|---|
| $k_2^{25}$(l mol$^{-1}$ s$^{-1}$) | very fast | | 8.2 | $2.8 \times 10^{-2}$ |
| p$K_a$(RH) | 37 | 36.5 | 41 | 35 |

| | $> C_6F_5$ | $> CH_2COOCH_3 \gg$ | $(CF_3)_3CH$ |
|---|---|---|---|
| | $2.5 \times 10^{-4}$ | $1.7 \times 10^{-6}$ | very slow |
| | 2 3 | 24 | 22 |

However, with further increase in the electronegativity of the group, for example in the case of $(CH_3COCH_2)_2Hg$, the reaction rate increases sharply and becomes almost the same as in the reaction with $(C_2H_5)_2Hg$; the order in electrophilic agent lies between 0 and 1. In all of the reactions the kinetic order in $R_2Hg$ is equal to 1 *.

In a previous communication [38], a high reactivity of organometallic compounds (in particular, of organotin compounds) containing fairly strong electron-accepting groups in electrophilic substitution reactions was explained by us by the fact that it is not the covalent form of the compound, but rather the ion pair, formed in the

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* See ref. 37 on the nucleophilic catalysis of the reaction by chloride ion.

pre-equilibrium step, that takes part in the reaction with the electrophilic reagent; i.e. by the ion-pair $S_E2$ mechanism, $S_E2$i.p.:

$$\mathrm{RSnMe_3} \underset{k_1}{\overset{k_1}{\rightleftarrows}} \mathrm{R^{-+}SnMe_3} \underset{k_2}{\overset{\mathrm{EN}}{\rightarrow}} \mathrm{RE + Me_3SnN}$$

This mechanism may be realized in the case where the nucleophilicity of R is not sufficiently high to accomplish direct electrophilic attack by the $S_E2$ mechanism, while the stability of the $R^-$ carbanion is insufficient for the $S_E1$ mechansim. Here attack by the electrophile on the ion pair in the limiting step of the reaction can prove to be energetically more favorable. As a result, if $k_{-1} \gg k_2[EN]$, the $S_E2$i.p. mechanism is realized; if $k_{-1} \ll k_2[EN]$, the $S_E1$ mechanism is realized. For strongly electron-donating R radicals it is possible to realize the classical $S_E2$ mechanism.

Organometallic chemistry makes it possible to vary the polarity of a C–M bond in the very wide range by changing the nature of the organic radical and the metal, and also the nature of the solvent. As it proved, the last factor exerts an especially great effect on the state of the studied organotin compounds in solution. Thus, some σ-bonded $RSnMe_3$ compounds, containing electron-accepting groups, are capable of not only ionizing, but also of dissociating in sufficiently polar solvents [39]. A study was carried out employing conductometry and UV and PMR spectroscopy. In non polar solvents, for example heptane, the electronic spectra of the 9-substituted fluorenyl and indenyl derivatives of $RSnMe_3$ almost coincide with the spectra of the corresponding RH hydrocarbons, which indicates the covalent character of the C–Sn bond in these compounds. The values of the $J(Sn{-}CH_3)$ constant in the PMR spectra of the 9-X-substituted derivatives of 9-fluorenylmethyltin (X = CN, $C_6H_5$, $CH_3$, H) in $CH_2Cl_2$ or $DCCl_3$ also testify to this fact. However, the electronic spectrum of $(9\text{-}CNC_{13}H_8)SnMe_3$ in hexamethylphosphotriamide (HMPTA) proved to be identical with the spectrum of the corresponding Cs salt [40], in which the position of the absorption maxima and the ratio of the extinction coefficients did not change with dilution, which indicated the formation of either free ions or solvate-separated ion pairs in solution, since the equivalent electrical conductivity remains practically constant when the concentration is varied in the range $(2{-}8) \times 10^{-3}$ *M*.

$$\mathrm{(9\text{-}CNC_{13}H_8)SnMe_3} \rightleftarrows \mathrm{9\text{-}CNC_{13}H_8{}^- + Me_3Sn^+}$$

The dissociation of $(9\text{-}CNC_{13}H_8)SnMe_3$ in HMPTA is also confirmed by the fact that when going from $CH_2Cl_2$ to HMPTA as solvent an increase in the $J(^{117,119}Sn{-}CH_3)$ coupling constant from 55.3/55.7 to 68.6/71.8 Hz is observed in the PMR spectra, in which connection the value of the $J(Sn{-}CH_3)$ coupling constant and the chemical shift in HMPTA coincide completely with the corresponding values of the ionic $Me_3SnBF_4$ in the same solvent. $(9\text{-}CNC_{13}H_8)SnMe_3$ in acetonitrile or pyridine is also capable of dissociating into the free ions, although this dissociation is not complete. In $CH_3CN$, for example, the degree of ionization is a total of 1.2% at a concentration of $6.8 \times 10^{-3}$ *M*. For the example of $(9\text{-}CNC_{13}H_8)SnMe_3$, when the nature of the solvent was varied it was shown that the dissociation of the organotin compound is determined by the donor capacity of the solvent, and not by its dielectric constant.

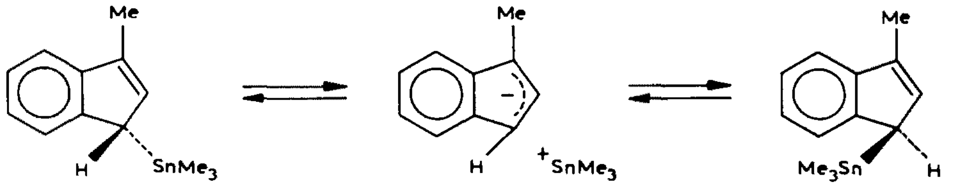
An important factor, determining the ability of $RSnMe_3$, to either ionize or dissociate, is the nature of the R group. It has been found that under the conditions employed the substituted fluorenyl derivatives of tin are capable of dissociating in HMPTA. Thus, their electronic spectra have the absorption bands of the corresponding fluorenyl carbanions. In the PMR spectra is observed a broadening of the signals, which indicates the existence of an equilibrium between the covalent and ionized forms in solution. An analysis of the spectra and their temperature dependence shows that the dissociation of the 9-X-substituted fluorenyl derivatives of tin decreases in the following order of the X substituents: CN > $C_6H_5$ > $CH_3$,H. The indenyl derivative of tin is incapable of ionization under the conditions studied, whereas (1-methyl-3-phenylindenyl)trimethyltin is dissociated completely in HMPTA. In general, the ability of $RSnMe_3$ to dissociate (or ionize) is determined by the stability of the R carbanion, as can be seen from the following p$K_a$ values of RH.

| R in $RSnMe_3$ | $C_{13}H_9$ | 9-$CH_3C_{13}H_8$ | $C_9H_7$ |
|---|---|---|---|
| p$K_a$(RH) | 22.1 | 21.8 | 20.2 |
| | Partial dissociation | | Does not dissociate |

| 9-$C_6H_5C_{13}H_8$ | 1-$CH_3$-3-$C_6H_5C_9H_5$ | 9-$CNC_{13}H_8$ |
|---|---|---|
| 18.6 | 16 | 11.4 |
| | Complete dissociation | |

However, some compounds dissociate to a greater degree than would be expected on the basis of their p$K_a$ values. Thus, (9-$C_6H_5C_{13}H_8$)$SnMe_3$ dissociates completely, while $C_9H_7SnMe_3$ does not dissociate noticeably, although the p$K_a$ of indenyl and 9-phenylfluorene are the same. Apparently, this is related to the effect of steric factors and a decrease in the steric strain during dissociation.

These results, which demonstrate the ability of these organotin compounds to ionize and dissociate, are undoubtedly an important argument in support of the possibility of the ion-pair mechanism $S_E2$ i.p. in those cases where the ions and ion pairs are not detected by other methods. Direct proof for the formation of ion pairs in the solution of the organotin compounds was obtained for this case as the result of stereochemical studies. The optically active *S*-(+)-(1-methyl-3-phenylindenyl)trimethyltin ($[\alpha]_D^{18}$ 232°, $C_6H_6$, *c* 2,4) and (+)-(1-methyl-3-phenylindenyl)trimethyltin ($[\alpha]_D^{18}$ + 24°, $C_6H_6$, *c* 4,4) were synthesized for this purpose [41,42]. These organotin compounds are quite stable in low-polar aprotic solvents ($C_6H_6$, dimethoxyethane (DME)), but they quickly racemize when HMPTA is added. It may be assumed that the loss of stereochemical configuration occurs as the result of ionization, which facilitates the coordination of the solvent at the Sn atom, with the formation of the ion pair, which returns to the starting state with racemization, for example:



The rate of racemization of these organotin compounds is found to agree with their ability to ionize. Thus, (1-methyl-3-phenyl)indenyltrimethyltin, which is more inclined to ionize, loses optical activity noticeably even in benzene ($k_1^{20} = 3.2 \times 10^{-5}$ s, $c$ 0.2 $M$), while the racemization proceeds even more rapidly in $CH_2Cl_2$. The racemization of (3-methylindenyl)trimethyltin under these conditions is extremely slow.

The ability of the organotin compounds studied to ionize, to react by the $S_E2$i.p. mechanisms (within the framework of which their high reactivity becomes understandable), can be used for synthetic purposes. This can be illustrated by citing the reaction of $RSnMe_3$ (R = 9-fluorenyl, 3-methylindenyl, indenyl, 9-cyano-9-fluorenyl) with alkylating agents ($CH_3I$, $CH_3OTs$, $(CH_3)_2SO_4$) in HMPTA [43]. It is known that the alkyldestannylation reaction is not characteristic for organotin compounds, but in the case of tin derivatives containing electron-acceptor groups, this reaction goes quite easily and completely in HMPTA.

$$RSnMe_3 + MeX \rightarrow RMe + Me_3SnX$$

In their reactivity in this reaction these organotin compounds fall into practically the same order as in the other electrophilic substitution reactions discussed above: $(9\text{-}CNC_{13}H_8)SnMe_3 \gg C_9H_7SnMe_3 > (3\text{-}MeC_9H_6)SnMe_3 \gg C_{13}H_9SnMe_3$. The reactivity of the methylating agents decreases in the order: $CH_3I > CH_3OTs > (CH_3)_2SO_4$. This effect of the nature of the leaving group is characteristic for nucleophilic substitution reactions involving "soft" nucleophilic agents.

Alkyldestannation is also quantitative under the influence of trityl fluoroborate in $CH_2Cl_2$ [44].

$$RSn(CH_3)_3 + (C_6H_5)_3CBF_4 \xrightarrow{CH_2Cl_2} (C_6H_5)_3CR + (CH_3)_3SnBF_4$$

$$R = CH_3,\ CH_2{=}CHCH_2,\ C_6H_5C{\equiv}C,\ C_9H_7,\ CN.$$

$RSnMe_3$ compounds, containing strong electron-accepting R groups ($C_6H_5C{\equiv}C$, $C_9H_7$, CN) proved to be especially active in this reaction, which is in complete agreement with the data discussed above for the other reactions.

In principle, a different mechanism is realized in the reaction of $C_6H_5Sn(CH_3)_3$ with $(C_6H_5)_3CBF_4$, in which benzene is obtained instead of the expected $(C_6H_5)_4C$. In this case the organotin compound is oxidized to give the phenyl radical, which cleaves an H atom from the solvent:

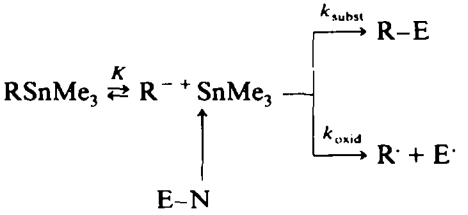
$$C_6H_5Sn(CH_3)_3 + (C_6H_5)_3CBF_4 \rightarrow C_6H_5^{\cdot} + (C_6H_5)_3C^{\cdot} + (CH_3)_3SnBF_4$$

$$C_6H_5^{\cdot} + CH_2Cl_2 \rightarrow C_6H_6 + CHCl_2^{\cdot}$$

A possible reason for this reaction is the steric hindrance created by the $Me_3Sn$ group to the formation of the σ-complex, which makes it impossible for the normal electrophilic substitution to be realized.

Another triarylmethyl salt, namely tris(*p*-nitrophenyl)bromomethane, exhibits both electrophilic and oxidizing properties in reactions with the organotin compounds [45,46]. However, the reaction proceeds only with $RSnMe_3$ compounds that contain electron-accepting R groups (9-fluorenyl, indenyl, cyclopentadienyl), and does not take place even with allyl- and phenyl-trimethyltin, which usually exhibit a high reactivity in $S_E2$ reactions.

In view of the fact that in this reaction both oxidation and electrophilic substitution are accelerated by an increase in the electronegativity of the R group, it may be assumed that both processes are accomplished with involvement of ion pairs that are formed in the pre-equilibrium step, apparently by the coordination of the nucleophilic portion of the electrophilic agent with the metal atom:



In this case both processes, oxidation and electrophilic substitution, proceed via a common ionization step. The yield of the oxidation and substitution products is determined by the ratio between the reducing ability of the ion pair ($k_{oxid}$) and its ability to undergo electrophilic attack ($k_{subst}$). Since when going to more stable $R^-$ carbanions the proportion of the redox process increases, it may be assumed that in the series of 9-fluorenyl-, indenyl-, and cyclopentadienyl-trimethyltin the reducing capacity of the $R^{-}\,{}^{+}SnMe_3$ ion pair decreases to a lesser degree than does its nucleophilicity. From these data it can be seen that the concept of the ion-pair mechanism is applicable not only to electrophilic substitution processes, but also to oxidation processes.

## Ions and ion pairs in alkylation by alkyl halides of alkali metal salts of CH acids

It is well known that the alkali metal salts of CH acids exist in solution as an equilibrium mixture of various ionic species (free anions, contact and solvate-separated ion pairs, associates of ion pairs). The equilibrium is shifted toward the different forms by varying the temperature and nature of the solvent or by replacing the cation, and also by adding either ionic or solvating additives to the solution. This fact has great importance, since in the general case the mentioned types of ionic species differ in their reactivity. Consequently, when studying the kinetics of the reactions of the alkali metal salts of CH acids it is possible to make correct conclusions as to their mechanism only when the character of the reacting species is established, their concentrations are known, and the contribution of each of them to the empirical rate of the process was measured. However, prior to the studies of the author and his coworkers, data were lacking on the reactivity of ionic species of diverse type even for the reactions of the alkali metal salts of CH acids with very simple electrophilic agents.

The reactions of the alkali metal derivatives of fluorene and its 9-substituted derivatives, and also of triphenylmethane and tris(*p*-nitrophenyl)methane, with alkyl halides were selected as the models [40,47,48]. The first step of the studies consisted in studying the state of these compounds in solution, i.e., in identifying the ionic species present and determining their concentrations, for which we employed conductometry and spectrophotometry in the visible and UV regions. A decrease in the solution concentration and its temperature, and the addition of solvating ionic fragments, causes an increase in the intensity of the bands that characterize the free anions. In turn, conductometry gives quantitative information on the amount of these species present. An increase in the intensity of the bands when alkali-metal tetraphenylborates are added indicates the presence of contact ion pairs in the solution. This is also indicated by a monotonic shift of the absorption bands of the organoalkali compound toward shorter wavelengths with decreasing size of the cation. The solvate-separated ion pairs are "de-excited" by crown polyethers and low temperatures. For example, the spectrum of the Li salt of tris(*p*-nitrophenyl)methane in THF, in the presence of various additives, gives an example as to what information can be obtained from the spectra of solutions of the alkali derivatives of CH acids. The starting spectrum characterizes the equilibrium mixture of contact ion pairs and free anions:

$$A^-M^+ \overset{k_D}{\rightleftarrows} A^- + M^+ \qquad (1)$$

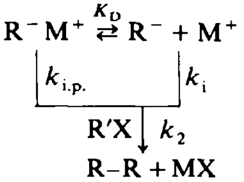
In the presence of lithium tetraphenylborate, which suppresses the dissociation of the Li salt, one broad band observed in the spectrum, which characterizes the absorption of the contact ion pairs. The addition of a crown polyether causes a sharp increase in the intensity of the log-wave band, caused by the absorption of the free anions. A similar effect is exerted by $(C_6H_5)_4AsCl$, since in this case ion exchange leads to the formation of the tetraphenylarsonium salt of tris(*p*-nitrophenyl)methane, which dissociates completely in THF, Similar procedures made it possible to establish that the ion pairs of the alkali salts of tris(*p*-nitrophenyl)methane, 9-cyanofluorene, and 9-carbomethoxyfluorene, and also of triphenylmethylcesium, in solvents of the ether type belong exclusively to the contact type, while the Li salts of fluorene, 9-methylfluorene, and triphenylmethane are represented by ion pairs of only the solvate-separated type. In turn, the structure of the anion and size of the cation determine the degree of dissociation of the ion pairs to the free ions, i.e., the dissociation constant of the corresponding salt (equilibrium 1). The following rules are observed here: 1) ion pairs of the solvate-separated type (triphenylmethyllithium) dissociate much more easily than the contact ion pairs (triphenylmethylcesium); 2) the dissociation constants of the lithium solvate-separated ion pairs of fluorene, 9-methyl-, and 9-phenyl-fluorene in DMF practically coincide, although in this series the $pK_a$ of the CH acids changes by more than four units; 3) the dissociation constant increases with increasing radius of the alkali metal cation.

When compared with the contact ion pairs, the high ability of the solvate-separated ion pairs to dissociate is fully explicable: the molecules of the solvent, found between the ionic fragments of such a pair, weaken the coulombic interaction of the latter substantially; a slight change in this interaction under the influence of structural factors also explains the observed effect of the alkyl or phenyl group attached to the carbanion center.

The dissociation constant of the contact ion pairs of the salts of tris(*p*-nitrophenyl)methane and 9-cyanofluorene increases in the order: $Li^+ < Na^+ < K^+ < Cs^+$. It should be mentioned that pure carbanion systems, in which the negative charge is delocalized on the C atoms, are characterized by an exact reciprocal relation between $K_D$ and the cation radius, since the driving force of the dissociation is solvation of the cation, which is expressed more strongly the higher the density of the positive charge on it. In the mesomeric 9-cyanofluorenyl and tris(*p*-

nitrophenyl)methyl anions the charge is localized mainly on the heteroatoms, on the N atom of the nitrile group in the first case and the O atoms of the nitro groups in the second case. Consequently, for these anions the effects of coulombic interaction in the ion pair predominate over the effects of cation solvation.

A study of the kinetics of the reactions of alkyl halides with the alkali metal salts of CH acids disclosed that both the ion pairs and the free anions are alkylated, i.e., the alkylation process can be described by the following scheme:



The reaction rate constants of the free anions $k_i$ and the ion pairs $k_{i.p.}$ were determined from the usual relationship between the observed rate constant $k_2$ and the degree of dissociation of the alkali metal salt, $\alpha$. A general rule is the higher reactivity of the free anions when compared with the ion pairs. The difference is especially great in the case where the ion pairs belong to the contact type. At the same time, the reactivity of the solvate-separated ion pairs is one half to one third that of the free carbanions. The reason for the decrease in the nucleophilicity of the anion in the presence of the cation is related to the fact that the latter facilitates the localization of the charge on a negatively charged species; this interferes with the formation of a new C–C bond or else it leads to an increase in the effective distance between the charged centers of the ions, thus weakening the coulombic interaction of the reactants. As a result, with a fixed structure of the anion an increase in the $k_i/k_{i.p.}$ ratio with increasing interaction of the fragments of the ion pair must be expected. In the reaction of the alkali metal salts of 9-cyanofluorene with ethyl iodide it is even possible to observe a linear relation between $\log(k_i/k_{i.p.})$ and the logarithm of the dissociation constant, which can serve as a measure of the strength of the ion pair.

The change in the reactivity of the free anion and ion pairs as a function of the alkylating agent, which is observed in the reactions of the alkali metal derivatives of 9-cyanofluorene, is characterized by the same rule: $k_i$ and $k_{i.p.}$ increase with a weakening of the C–Hal bond in the order: Cl < Br < I, and with an increase in the effective positive charge on the $\alpha$-carbon in the order: $C_4H_9 < C_3H_7 < C_2H_5 < CH_3$.

Among the most important factors which determine the reactivity of the anion, its basicity, a measure of which is the $pK_a$ of the starting CH acid, and also how strongly the anion is solvated in solution. For the anions of the substituted fluorene $k_1$ increases steadily with increase in the $pK_a$, and in the ordinates of $\log k_i$ vs. $pK_a$ the correlation is almost linear. The nucleophilicity of the anion is quite dependent on the strength of the solvate shell surrounding it. In the series of dipolar aprotic solvents an increase in the specific solvation of the 9-cyanofluorenyl anion, which can be characterized by the position of its absorption band, leads to a decrease in the reactivity, and here the change in $k_i$ corresponds to the change in the activity coefficient of the anion.

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