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SOLVENT EFFECTS ON THE REACTIVITIES OF ORGANOMETALLIC COMPOUNDS

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CONTENTS

A. INTRODUCTION

The role of a solvent on organometallic substitution reactions cannot be overestimated; even a small modification of the solvent structure may cause a large change in the rate and in the pattern of the processes in solution [1]. In the regrettable absence of systematic studies no leading chemical theory on the diversified solvent effects has been developed.

The limitations of the elementary electrostatic theory, which has been developed from the behaviour of aqueous salt solutions, have been emphasized recently [2,3]. For example the role of the dielectric constant and that of the solvent polarity as represented by the dipole moment μ are vastly overrated. The Debye—Hückel theory is an approximation for dilute aqueous salt solutions and cannot be extended to concentrated solutions and to most non-aqueous systems. It is therefore surprising to find that in non-aqueous media elementary electrostatic considerations are still widely used, in as much as it has been realized for some time that both nucleophilic and electrophilic interactions play a decisive role in the course of substitution reactions in organic and organometallic chemistry, as well as in ionization equilibria involving covalent substrates [2—6].

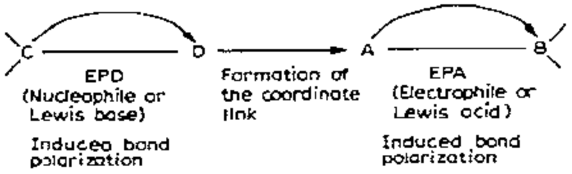
Indeed, many chemists may find themselves in conflict when choosing between quantitative and physically meaningful concepts and a qualitative appreciation of chemical effects on the grounds of systematic chemistry.

The author believes that each of these different approaches is extremely valuable in meeting the requirements of different aspects of chemistry. The theoretical and physical interpretation of structural data has contributed enormously to the advancement of chemistry. However, structural knowledge in itself is insufficient to understand chemical reactivity, as the functional properties depend to a great extent on the immediate environment [3,4,7]. Application of structural studies to the reactants, solvents, products as well as to transition states is very promising and it is in this area of chemical dynamics where structural and kinetic studies combine to give an appreciation of reaction mechanism, that coordination chemistry has much to offer.

Although molecular complexes are considered as intermediates in the course of chemical reactions [8,9] there have been very few systematic studies of the chemical effects in complexing. Preconceived ideas on the definition of chemical bonding and later the success of the Mulliken VB-theory for charge-transfer complexes have prevented the acceptance of the assumption made by Bennett and Willis [10] as early as 1929, according to which the union within a molecular compound is by means of covalent linkages. Even 35 years later the following statement is found [9]: "For a variety of reasons, including the fact that X-ray diffraction studies have clearly established that the separation distances between the solid complex components far exceed normal covalent bond lengths, this proposal need no longer be considered seriously".

It has recently been pointed out that there are indeed no principal differences between "weak" and "strong" coordinating interactions [7]. The distinction is, however, frequently made and weak molecular adducts are also known as "charge-transfer" complexes. It would be more correct to speak of "complexes showing-C-T-adsorption" as the term "charge-transfer" should not imply that transfer of charge is the major mode of binding in these complexes.

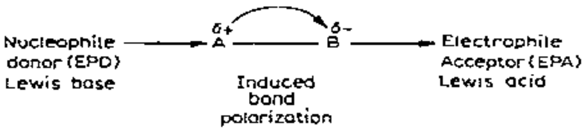
One of the most important conclusions of Lindqvist's theory of the coordinate bond [11] is that the formation of a coordinate link induces polarization and hence weakening of the adjacent σ-bonds both in the electron pair donor (EPD)- and electron pair acceptor (EPA)-units [7,11] within the new molecular adduct:



It should be emphasized that even small induced changes in bond polarity may be reflected in drastic changes in chemical reactivity. Most solvent effects as well as catalytic effects can be regarded as due to even small induced changes in bond properties in the intermediate molecular complexes [7—9] which can be followed by structural and spectroscopic methods.

The induced polarization of the bond A—B may take place in one of the following ways [2,5,6]:

(a) by nucleophilic attack at A,
(b) by electrophilic attack at B,
(c) by both effects at the same time (combined nucleophilic and electrophilic attack, cooperative effects).

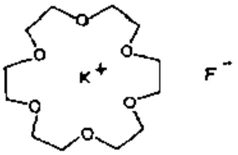


The extent of induced polarization for a given bond A—B depends on the strengths of the coordinate bonds with the nucleophile and (or) the electrophile: the stronger the coordinating interactions the greater the induced bond polarization, which may finally result in heterolysis [5,6].

A certain bond polarity within a functional group of the molecular adduct may be required for the occurrence of a substitution reaction. The suitable bond polarity may be obtained either by a proper solvent or by a catalyst. In this way a molecular adduct may be formed, which may be considered as the result of the sum of nucleophilic and electrophilic actions at the substrate.

Heterolysis is taking place when the ionic species are more stable (due to solvation = coordination) than the molecular adduct. Heterolysis by nucleophilic attack at A is connected with stabilization of the cation A^+ by coordination with the nucleophile [5,6,12]. Heterolysis by electrophilic attack at B is connected with stabilization of the anion B^- by coordination with the electrophile [5,6,12].

Since the coordinating properties of an ion are decreased by solvation a highly reactive ion should be practically unsolvated. This is only possible when the counter ion is highly stabilized: For example unsolvated ("naked") fluoride ions are available in solutions of KF even in benzene or acetonitrile in the presence of 18-crown-6, which strongly solvates the potassium ion. The unsolvated fluoride ion is a strong nucleophile and base and provides a facile and efficient means of obtaining organic fluorine compounds in high yield [13].



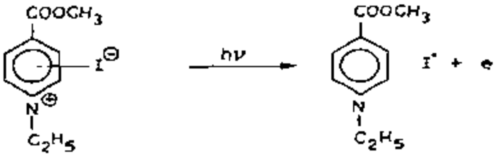
Thus, reactive anions are available in systems where only cations are strongly stabilized by coordination, e.g. in a strongly nucleophilic environment of extremely low electrophilic properties [3,5,6,13—15]. Likewise a highly reactive (unsolvated) cation may be available in a strongly electrophilic environment of extremely low nucleophilic properties, by which the anions are stabilized correspondingly [15].

The strongly amphoteric properties of water lead to stabilization of both cations and anions and hence the stabilities of many complex species are lower than in various non-aqueous media. On the other hand in a poorly coordinating medium the stability of the ionic species will be smaller than that of possible substitution products, e.g. substitution reactions may occur immediately after or even before the ions have actually been formed.

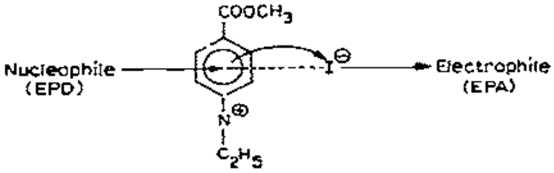
The main problems in discussing solvent effects have been (a) the difficulty in assigning increments for the nucleophilic and electrophilic contributions respectively, (b) the choice of proper empirical parameters for the nucleophilic as well as for the electrophilic functions (c) the difficulty in establishin the reaction mechanism and (d) as for the present discussion the choice of illustrative examples, which is somewhat arbitrary.

B. EMPIRICAL SOLVENT PARAMETERS

With the aim of establishing a phenomenological quantity for the "solvent polarity" in organic and organometallic interactions Kosower [8,16—18] suggested the so-called *Z*-value. This value is based on the UV-spectra of 1-ethyl-4-carbomethoxypyridinium iodide, the charge-transfer transition energy of this salt in a particular solvent being adopted as an empirical measure of the solvent polarity:



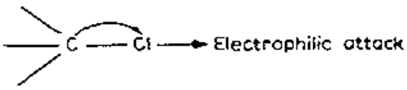
The charge-transfer energy expresses the difference between excited and ground state of the complex and therefore is a characteristic property of the complex as a whole (in the particular environment) and not a perturbed transition of either component [19]. Moreover it would be difficult to interpret the interaction of a solvent with this particular compound from the point of view of coordination chemistry. A considerable contribution to the polarization of the pyridine—iodine bond will be provided by the electrophilic solvent properties towards the iodide ion and this is in agreement with the close correspondence in the transition energy differences for iodide ion and the alkylpyridinium iodide [9]. In addition to this effect a strongly nucleophilic solvent, such as water may slightly interact with the aromatic nucleus and the sum of both the nucleophilic effect at the organic body and the electrophilic effect at the iodide will determine the actual state of polarization of the bond to iodine and hence the properties of the species in a particular solvent:



Grunwald et al. [20,21] suggested the so-called Y-values as a measure of the ionizing power of a solvent. They related the rate constants for the solvolysis of t-butyl chloride in a solvent under consideration k^{BuCl} to that in the reference solvent 80% aqueous ethanol k_o^{BuCl}:

$$Y = \log\,[k^{\mathrm{BuCl}}/k_o^{\mathrm{BuCl}}]$$

The ratio of the solvolysis reaction of t-butyl chloride is highly influenced by the electrophilic properties of the solvent attacking at the chlorine atom, by which the carbon—chlorine bond is polarized and weakened accordingly:



The close relationship between Z-values and Y-values found in a number of systems, has been taken as further support for the Z-values [8], which are much more convenient to measure than Y-values. Unfortunately they do not represent the nucleophilic properties: nearly identical Z-values are assigned to solvents of vastly different nucleophilic properties, such as nitromethane, acetonitrile and DMSO or diethylether and benzene. Hence numerous cases have been found, where the application of the Z-values failed.

The same is true for the E_T-values proposed by Dimroth and Reichardt [22—24], which are based on the solvent sensitivity of the light absorption (an intramolecular charge-transfer transition) of a pyridinium phenol betaine.

The supposed advantage of a solvent polarity parameter based on a physical process which is believed to be understood in great detail no longer remains when different chemical changes are considered. From the point of view of coordination chemistry it is essential to make a distinction between nucleophilic (donor) properties and electrophilic (acceptor) properties and to introduce empirical functional parameters to each of them.

For the nucleophilic properties of a solvent the best empirical parameter available is the donicity, which is defined as the negative ΔH-value in kcal. mol^{-1} for the interaction of the electron pair donor with SbCl$_5$ in a highly

TABLE 1

Donicities *DN* and dielectric constants ϵ of several donor solvents

Solvent	DN [kcal. mol^{-1}]	ϵ
1,2-Dichlorethane	—	10.1
Benzene	0.1	2.3
Sulfurylchloride	0.1	10.0
Thionylchloride	0.4	9.2
Acetylchloride	0.7	15.8
Tetrachloroethylene carbonate (TCFC)	0.8	9.2
Benzoyl fluoride (BF)	2.3	23.0
Benzoyl chloride	2.3	23.0
Nitromethane (NM)	2.7	35.9
Dichloroethylene carbonate (DEC)	3.2	31.6
Nitrobenzene (NB)	4.4	34.8
Acetic anhydride	10.5	20.7
Phosphorus oxychloride	11.7	14.0
Benzonitrile (BN)	11.9	25.2
Selenium oxychloride	12.2	46.0
Acetonitrile (AN)	14.1	38.0
Sulpholane (tetramethylenesulfone, TMS)	14.8	42.0
Dioxan	14.8	2.2
Propanediol-1,2-carbonate (PDC)	15.1	69.0
Benzylcyanide	15.1	18.4
Ethylenesulphite (ES)	15.3	41.0
iso-Butyronitrile	15.4	20.4
Propionitrile	16.1	27.7
Ethylenecarbonate (EC)	16.4	89.1
Phenylphosphonic difluoride	16.4	27.9
Methylacetate	16.5	6.7
n-Butyronitrile	16.6	20.3
Acetone (AC)	17.0	20.7
Ethylacetate	17.1	6.0
Water	18.0 (33.0 [a])	81.0
Phenylphosphonic dichloride	18.5	26.0
Diethylether	19.2	4.3
Tetrahydrofurane (THF)	20.0	7.6
Diphenylphosphonic chloride	22.4	—
Trimethylphosphate (TMP)	23.0	20.6
Tributylphosphate (TBP)	23.7	6.8
Dimethoxyethane (DME)	≈24	7.2
Dimethylformamide (DMF)	26.6	36.1
N-methyl-ϵ-caprolactam (NMC)	27.1	—
N-methyl-2-pyrrolidinone (NMP)	27.3	—
N,N-Dimethylacetamide (DMA)	27.8	37.8
Dimethylsulphoxide (DMSO)	29.8	45.0
N,N-Diethylformamide (DEF)	30.9	—
N,N-Diethylacetamide (DEA)	32.2	—
Pyridine (py)	33.1	12.3
Hexamethylphosphoramide (HMPA)	38.8	30.0
Hydrazine	44.0 [a]	51.7

TABLE 1 (continued)

Solvent	DN [kcal. mol^{-1}]	ϵ
Ethylenediamine	55.0 [a]	14.2
Ethylamine	55.5 [a]	6.9
Isopropylamine	57.5 [a]	6.0
t-Butylamine	57.5 [a]	6.0
Ammonia	59.0 [a]	17.0
Triethylamine	61.0	—

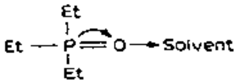
[a] Bulk donicity e.g. the donicity of the solvent in the associated liquid [3]

diluted solution of dichloroethane [15,25]:

$$DN \equiv -\Delta H_{\mathrm{EPD.SbCl_5}}$$

The donicities of Lewis bases have been found to be related to various empirical properties as long as their electrophilic properties are poorly developed. Indeeed we shall see later (Table 2) that most aprotic solvents have poor acceptor properties and hence their donicities are proportional to the chemical shifts observed in the acceptor component of charge transfer complexes and in adducts [26], to the extent of charge transfer involved in ion solvation [27], to the values for the redox-potentials for a given redox system in different aprotic solvents [3,28], as well as to kinetic parameters [29].

For the electrophilic solvent properties a qualitative order has been obtained from anion solvation studies [30,31]. A quantitative parameter has been derived from the ^{31}P NMR shifts produced in triethylphosphine oxide by the electrophilic solvent actions [32] which lower the electron densities at the P-atoms due to inductive effects [7]



$$\mathrm{Et-\overset{Et}{\underset{Et}{P}}=O\rightarrow Solvent}$$

The δ-values have been related to those of the $\mathrm{(Et)_3PO\rightarrow SbCl_5}$ adduct dissolved in 1,2-dichloroethane, which has been arbitrarily taken to have the value of 100. These values have been termed "Acceptor Numbers" *AN* and they represent dimmensionless numbers expressing the acceptor properties of a given solvent relative to those of $\mathrm{SbCl_5}$, which is also the reference substance for assessing the donicities.

One of the most remarkable results presented in Table 2 [32] is the extremely low electrophilic character of diethylether, while the non-polar solvents benzene and carbon tetrachloride have stronger electrophilic properties, which are not drastically different from most other aprotic solvents. Considerably greater acceptor numbers are found for solvents containing acidic C-H-hydrogen atoms such as CH_2Cl_2, $CHCl_3$ or formamide. As expected, higher values are found for the alcohols and for water and to a greater extent for protonic acids.

It can be seen from Table 2 and it has been shown in more detail [32] that fair relationships exist between E_T-values, Z-values and the acceptor numbers. Hence the former are not representing a general measure of the

TABLE 2

^{31}P NMR-shifts of Et_3PO referred to Et_3PO in hexane in different solvents, accepor numbers AN, the Dimroth-Reichardt E_T-values and Kosowers Z-values for the respective solvents

Solvents	$\delta^{31}P$ [ppm]	AN	E_T [kcal mol^{-1}]	Z [kcal mol^{-1}]
Hexane (Reference Solvent)	0	0	30.9	
Diethylether	−1.64	3.9	34.6	
Tetrahydrofurane (THF)	−3.39	8.0	37.4	58.8
Benzene	−3.49	8.2	34.5	54.0
Carbon tetrachloride	−3.64	8.6	32.5	—
Diglyme	−4.20	9.9	—	—
Glyme	−4.35	10.2	38.2	59.1
HMPA	−4.50	10.6	40.9	62.8
Dioxane	−4.59	10.8	36.0	
Acetone	−5.33	12.5	42.2	65.5
N-methyl-2-pyrrolidinone (NMP)	−5.65	13.3	42.2	
DMA	−5.80	13.6	43.7	66.9
Pyridine	−6.04	14.2	40.2	64.0
Nitrobenzene (NB)	−6.32	14.8	42.0	
Benzonitrile (BN)	−6.61	15.5	42.0	65.0
DMF	−6.82	16.0	43.8	68.5
Dichloroethane carbonate (DEC)	−7.11	16.7	41.9	63.4
PDC	−7.77	18.3	46.6	
CH_3CN	−8.04	18.9	46.0	71.3
DMSO	−8.22	19.3	45.0	71.1
CH_2Cl_2	−8.67	20.4	46.1	64.7
Nitromethane (NM)	−8.74	20.5	46.3	71.2
$CHCl_3$	−9.83	23.1	39.1	63.2
i-Propanol	−14.26	33.5	48.6	76.3
Ethyl alcohol	−15.80	37.1	51.9	79.6
Formamide	−16.95	39.8	56.6	83.3
Methyl alcohol	−17.60	41.3	55.5	86.3
Acetic Acid	−22.51	52.9	51.2	79.2
Water	−23.35	54.8	63.1	94.6
CF_3COOH	−44.83	105.3		
CH_3SO_3H	−53.77	126.3		
$SbCl_5$ as reference in DCE	−42.58	100		

polarity or of the ionizing properties of a solvent, but rather bear a close relationship to the electrophilic properties of the solvent. It has been rather unfortunate that Kosowers correct ideas about the formation of molecular adducts as a result of solute—solvent interactions could not be applied widely as he failed to recognize the chemical meaning of his polarity scale as an approximate guide for the relative electrophilic character of the solvents. The frequent use of the terms "solvent polarity" and "ionizing power of a solvent" as synonymous expressions [18] has been particularly unfortunate and misleading, since there is no general relationship between solvent polarity (denoting the dipolar character of solvent molecules or more precisely, the distribution and polarizability of the charges) and ionizing properties (the ability of the solvent to heterolyze covalent bonds). The latter have clearly been shown to depend on the nucleophilic and on the electrophilic properties of the solvent towards the substrate [4,6]. It is therefore important to recognize the functions involved and to estimate their respective contributions.

Close relationships exist also between the acceptor numbers and thermodynamic quantities such as the free energies of solvation of halide ions [32] or the redox potentials of the hexacyanoferrate(III)-hexacyanoferrate(II)-system [32,33].

The reactivities of solutes greatly depend on the nucleophilic and electrophilic interactions with the solvent. In a donor solvent the nucleophilic properties of the substrate are enhanced the greater its donicity, as long as the solvent is not acting as an electrophile at the same time. On the other hand a strongly electrophilic solvent without simultaneous nucleophilic attack at the substrate will strongly increase the electrophilic character of the latter. It may be concluded that the formation of reactive anions is favoured in a solvent of high donicity and low acceptor number, while the formation of reactive cations is best achieved in a solvent of low donicity and of high acceptor number.

C. CARBANION REACTIVITY AND STABILITY OF COUNTER-IONS

The high reactivities of organolithium compounds are usually regarded as due to the high polarities of the lithium—carbon bonds. The polarities of the corresponding sodium or potassium compounds are considered even higher but their reactivities in solution are usually lower than those of the lithium compounds.

These differences are readily accounted for by considering the different electrophilic properties of the alkali metal ions: the lithium ion is a stronger Lewis acid than any other alkali metal ion and is more strongly solvated by a given donor solvent, in which the lithium—carbon bond is more strongly polarized and more easily heterolyzed than the corresponding potassium—carbon bond. By increasing cation—solvation the cation—anion interactions are weakened and hence the activities of the carbanions are enhanced. The extent of bond polarization may be considered as the result of both the solvent EPD-properties as represented by the donicity [15] and the Lewis acid properties of the metal ions.

The normal acidity of the metal ions and the reactivities of their organometal compounds decreases in the order [34]:

$Be > Mg > Li > Ca > Na > Sr > Ba > K > Rb > Cs > R_4N$

This behaviour is also known for inorganic salts: lithium iodide has a higher conductivity in HMPA and hence is more strongly ionized than a tetraalkylammonium iodide in the same solvent [14]. In this solvent the cations are strongly solvated (*DN* = 38,8). Since lithium ion is a stronger Lewis acid than a tetraalkylammonium ion (see the series above), the size of the $[Li(HMPA)_n]^+$ ion is greater and hence cation—anion interactions weaker than in the case of the tetraalkylammonium ion; this means that the ionization of the Li-salt solution is greater than that of the tetraalkylammonium salt.

HMPA has a donicity of 38,8, while its anion solvating properties as expressed by the $\Delta\delta^{31}P$ NMR-shifts are as weak as those of dioxane or acetone (Table 2). A halide ion remains nearly unsolvated in this solvent and acts as a stronger base than in donor solvents of greater EPA-properties. Benzylmagnesium bromide gives a red solution, as it is ionized to strongly coordinated $MgBr^+$-cations and unsolvated benzyl anions [35].

The tetraphenylborate ion is practically unsolvated in all solvents. The cesium salt shows different behaviour in THF and in dimethoxyethane (DME), the dissociation constant being twenty times greater in DME than in THF although the solvent dielectric constants are nearly identical [1]. In THF the cesium ion is nearly uncoordinated, while it is coordinated by DME-molecules. Both of these effects may be rationalized by the donicity concept: the higher *DN* of DME stabilizes the cations, enhances the dissociation and hence the concentration of the unsolvated anions. However, to account for the behaviour of $Na^+BPh_4^-$ it is necessary to assume that both in THF and DME the salt forms solvent coordinated Na^+-ions [1], indicating that the Na^+ ion is a stronger Lewis acid than the Cs^+-ion.

Methyllithium is tetrameric in the solid state: four lithium atoms form a tetrahedron with methyl groups at each of its faces [36], so that each lithium atom is coordinated to three methyl groups. The tetrameric structure also prevails in benzene solution. Addition of base molecules leads to coordination to each of the lithium positions [37] with subsequent polarization of the lithium—carbon bonds (Fig. 1).

The extent of metal—carbon bond polarization and that of ionization in solution depends on the solvent base strength following the order of the donicities (Table 1), as long as their electrophilic properties are weak (Table 2):

benzene < diethylether < THF < Me_3N < py < HMPA [34,38,39]

Even more stable are the complexes with chelating ligands, such as tetramethylethylenediamine or 2,2'-bipyridyl [40].

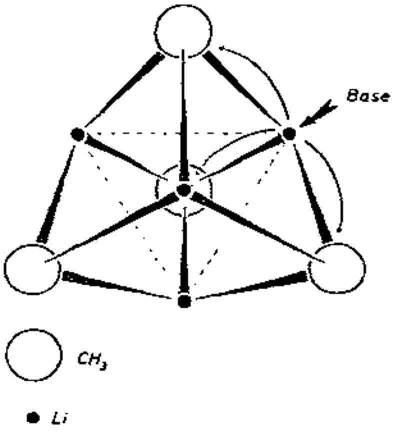
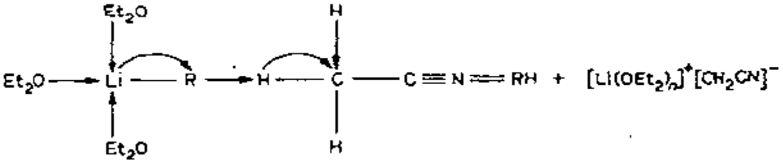


Fig. 1. Bond polarization in $(LiCH_3)_4$ by one base molecule.

Ethyl sodium has a layer structure [41] and methyl potassium is coordinated by six methyl groups and the bonds are believed to be more ionic than in the lithium compound. It has been pointed out that in solution in donor solvents the lithium compound gives more stable cations and hence is more reactive in carbanion induced reactions, as long as the solvent has weak anion solvating properties.

The different reactivities of organolithium compounds in solvents of different donor properties are seen from the following example: aliphatic nitriles [43] and aliphatic ketones [44—46] are deprotonated by organolithium compounds in diethylether, while no reaction is observed in petrol ether. Coordination at the lithium by diethyl ether molecules induces a strong polarization of the Li—C-bonds possibly yielding carbanions separated from the cations by ether molecules coordinated to the lithium ions. The carbanions remain unsolvated in diethyl ether and are readily available for attacking the methyl groups of a nitrile or of a ketone with deprotonation.

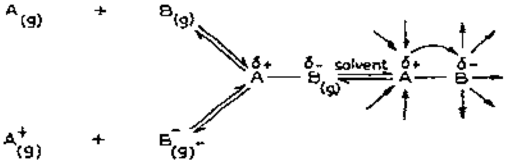


$$Et_2O \rightarrow \overset{Et_2O}{\underset{Et_2O}{Li}} - R \rightarrow H - \overset{H}{\underset{H}{C}} - C \equiv N \longrightarrow RH + [Li(OEt_2)_n]^+[CH_2CN]^-$$

In petrol ether (low EPD- and low EPA-properties) the Li—R species remains unionized and in this state the organic group bound to the lithium is not sufficiently reactive in order to permit the occurrence of an analogous reaction.

The loosely bonded ions in diethyl ether have been termed "solvent-separated ion pairs" in order to distinguish them from another type of ion pair, the so-called "intimate" or "contact ion pairs". These have been postulated in order to explain the stereochemical course of solvolysis and of electrophilic substitution reactions [47—52]. Since then the existence of both types of ion pairs has been widely accepted and supported by results obtained by various physico-chemical methods, such as UV spectroscopy, conductivity measurements and electron spin resonance [53—58]. In "contact ion pairs", cations and anions are considered to be in immediate contact with each other.

It must be anticipated that the properties of a bond between two atoms do not depend on the mode of its formation. For example the properties of the H—F-molecule will not allow a decision whether it has been formed from the atoms or from the hydrogen ion and fluoride ion. Hence solvation in a particular solvent is also independent from the history of the solute, which leads to a greater extent of bond polarization than is observed in the gaseous molecule [7]. It is not possible, however, to distinguish by experiment between a solvated "contact ion pair" and an unionized solvated species:



"contact ion pair"
or
"unionized species".

The limiting case of a real "contact-ion pair" is found in solutions to which the "sphere in continuum model" can be applied, e.g. where neither cation nor anion are solvated, such as for $[Bu_4N]^+[BPh_4]^-$ solutions [3]. We shall examine now the validity of the statements made above.

Hogen-Esch and Smid [53,54] investigated the formation of "contact ion pairs" of alkali metal salts of various carbanions and radical anions in a number of solvents. Their results show that the stabilities of the contact ion pairs are decreased as the donicities of the solvent molecules increase and this represents the typical behaviour of covalent substrates. In a solvent of high donicity such as pyridine or DMSO only solvent separated ion pairs and free ions are present, while the unionized species (contact ion pairs) is found in a weak donor solvent such as toluene.

The results for alkali metal—fluorenyl compounds are given in Table 3. It can be seen that the extent of ionization depends on the nature of the alkali metal ion, the lithium compounds being more easily ionized (due to their greater Lewis acid strength) than the other alkali metal ions. It is further supported by increase in solvent donicity and not, as has been supposed, by the increase in dielectric constant.

Structural investigations have established that in the solid lithium fluorenyl-THF-adduct the carbanionic electron pair is bonded to the lithium despite the delocalization in the aromatic system. Three tetrahydrofuran molecules are bonded to each lithium, while the fourth ligand position is occupied by the carbanionic ligand [59]. The ionization of naphthaline sodium is drastically

TABLE 3

Amount of solvent separated ion pairs (+free ions) of alkali metal salts of 9-fluorene (Fl) in various solvents at 25° [53,54]

Solvent	% Solvent-separated ion pairs (+free ions)				
	DN	ϵ	Li^+Fl^-	Na^+Fl^-	Cs^+Fl^-
Dioxan	15	2.2	0	0	0
Toluene	0.1	2.4	0	0	0
2-Me-THF	18	6.3	25	0	0
THF	20	7.6	75	5	0
DME	≈24	7.2	100	95	0
DMSO	29.8	45.0	100	100	—
Pyridine	33.1	12.3	100	100	—

increased by changing from THF to glycoldimethylether [60—62].

Styrene lithium gives solvent-separated ion pairs in THF: the polymerization of styrene is considerably faster in THF (*DN* ≈ 20) than in dioxane (*DN* = 14,8), although the dielectric constants of the two solvents are nearly identical. In dioxane the pattern is reversed, the cesium compound being more reactive than the lithium compound [62,63]. This shows that the Cs—carbon bond is more polar than the Li—carbon bond in the weakly solvated state, while a stronger solvating solvent mobilizes the carbanion from the lithium compound to a greater extent due to the greater Lewis acid strength of the Li^+-ion and the greater ease of polarization of the Li—C-bond. The absorption maximum of 1,1-diphenyl hexyl lithium is shifted to longer wave lengths [64—66] by increasing solvent donor properties (Table 4).

The effects of cation solvation can also be seen from IR-work. In solvents of medium EPD-strength, such as THF [67,68] or acetone [69], the band frequencies of lithium, sodium and potassium ions are dependent on the anion; in contrast, in strong EPD-solvents, such as DMSO [70,71] 1-methyl-2-pyrrolidone [72,73] and pyridine [74], the frequencies are nearly independent of the anion. This was ascribed to the presence of solvent-separated

TABLE 4

Absorption maxima of 1,1-diphenyl hexyl lithium in donor solvents

Solvent	*DN*	λ max [nm]
Benzene	0.1	425
Diethylether	19	488
THF	20	496

ion pairs and free ions in the strong EPD-solvents and of "contact ion pairs" in THF and acetone.

Popov and coworkers [69,71] demonstrated that variations of band frequency on changing the anion, as observed in THF and acetone, cannot be ascribed to the rather low dielectric constants of these solvents, but are due to their moderate solvating power. For example, nearly constant frequencies are observed for lithium salts independent from the anion in mixtures of benzene and DMSO with dielectric constants ranging from 7 to 46 [71], in which the lithium ions are coordinated by DMSO molecules. Wuepper and Popov [73] dissolved alkali metal salts in dioxane, added DMSO to the solution and found the same characteristics as in pure DMSO. Despite the low dielectric constant of the dioxane solution, the high donicity of the added DMSO gives DMSO-solvates of the alkali metal ions and the solvation sphere is no longer penetrable by anions competing for coordination.

Valuable information is further provided by studies of the lithium fluorenyl in mixtures of acetone and nitromethane (NM) [69]. In these mixtures the intensity of the band observed at 425 cm^{-1} and assigned to the stretching motions of the Li^+—O-coordinate bonds is a linear function of the mole ratio acetone/$LiClO_4$ provided that the mole ratio is <4. It was concluded that under these conditions Li^+ is coordinated by four molecules of acetone. Preferential solvation of the lithium ion by acetone is readily understood by comparing the donicities of the two solvents: $DN_{\text{acetone}} = 17{,}0$, $DN_{\text{NM}} = 2{,}7$, whereas elementary electrostatic considerations are not helpful: NM has a higher dipole moment ($\mu = 3{,}57$ D) than acetone ($\mu = 2{,}88$ D) [75]. Raman and NMR results were explained by the formation of contact ion pairs at mole ratios acetone/$LiClO_4 < 4$ with $[ClO_4]^-$ ions entering the coordination sphere of the lithium ions; in other words they indicate the presence of solvated unionized lithium perchlorate. It has further been demonstrated that the perchlorate ion acts as an inner-sphere ligand in nickel- and cobalt-complexes only in solvents of moderate donicity [76].

The influence of various anions on the position of the Li^+ and Na^+ solvation bands was also investigated in acetone [69]. With perchlorates, tetraphenylborates, thiocyanates, nitrates and iodides, band frequencies are independent of the nature of the anion. For bromides and chlorides a shift to lower frequencies is observed. Adding $[Bu_4N]^+[ClO_4]^-$ or $[Bu_4N]^+I^-$ to solutions of $LiClO_4$ or LiI again does not change the bands but a shift to lower frequencies occurs on addition of $[Bu_4N]^+Br^-$ or $[Bu_4N]^+Cl^-$.

Selective solvation of various cations was studied in recent years in mixtures of water with solvents such as dioxane, tetrahydrofuran, acetonitrile, propanediol-1,2-carbonate and pyridine [77—83]. Except for pyridine—water mixtures, cations are preferentially solvated by water.

Relatively little is known about competitive solvation in mixtures of nonaqueous solvents. Complex formation between Na^+ and THF in solutions of $Na^+[AlBu_4]^-$ in hexane at molar ratios 1 : 1 and 1 : 4 was reported by Schaschel and Day according to proton NMR, as well as IR, and conductivity

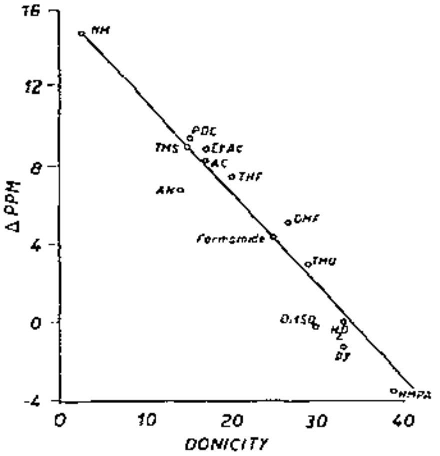


Fig. 2. Plot of infinite dilution sodium chemical shifts of $NaClO_4$ in different solvents vs. solvent donicities.

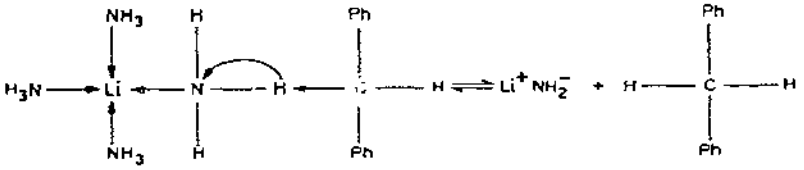
measurements [84,85]. Preferential solvation of alkali metal ions by DMSO occurs in 1-pentanone and by acetone in nitromethane [69,86].

A very remarkable relationship exists between solvent-donicity and chemical shift of the ^{23}Na-nucleus [27] in solutions of sodium perchlorate or sodium tetraphenylborate in various EPD-solvents (Fig. 2). It should be emphasized, that this relationship does not hold for solutions of sodium iodide, in which the chemical shift depends on the concentration of the salt, the effect being greater with decrease in solvent donicity. Again, the formation of contact-ion pairs has been postulated, e.g. replacement of solvent molecules by iodide ions in the inner solvation core around the sodium ion and hence the species is identical with solvated sodium iodide molecules in the respective solution, where the Na—I-bonds are more strongly polarized than in the gas phase [7].

It is frequently stated that the formation of solvent-separated ion pairs is greatly facilitated by increased solvent "polarity". Often, small changes in solvent structure can also drastically affect the equilibria under consideration [52]. It has further been recognized that, contrary to previous belief, solvent polarity per se does not affect the spectrum of the ion pair if its structure is retained [51]. The spectra of unionized species in solution are virtually indistinguishable from the spectra of the contact ion pairs, which are different from the spectra of solvent separated ion pairs. In addition to that, outer-sphere-complexes between ions of opposite charges are possible [29] which may be recognized by various methods [33]. For example, Warhurst and coworkers [87—89] observed in dioxane that increased size of the counter-ions leads to a bathochromic shift in the spectra of negative radical ions derived from aromatic hydrocarbons and ketones. For alkali salts the increase in the absorption frequency corresponding to λmax was found to be linear with $(r + \text{const})^{-1}$, r denoting the radius of the cation. Increase in r of alkali metal ions corresponds to a decrease in Lewis acidity and hence the bathochromic shift increases with increasing Lewis acidity of the metal ion suggesting the formation of outer-sphere complexes between ions of opposite charge [9]. Usually, the spectral studies provide information about the equilibria between non-ionized species ("contact ion pairs") and ionized species, e.g. the sum of solvent separated ion pairs and of free ions. Most equilibria hitherto interpreted by the presence of contact ion pairs, are better considered as "incomplete ionization".

The different behaviour of diphenylmethyl lithium and diphenylmethyl potassium in liquid ammonia is also readily explained by the different electrophilic properties of the lithium and potassium ions:

Diphenylmethyl—potassium is not decomposed by liquid ammonia [90], while the lithium compound is solvolysed to give lithium amide and diphenylmethane [34,91]. Those remarkable differences have been regarded as due to the differences in charge densities at the 1,1-diphenylmethyl carbanion and at the amide ion [34] and they may be better interpreted in the following way. The lithium compound is subject to considerable solvation at the metallic center with formation of carbanions, which interact with coordinated ammonia molecules with hydrogen bond formation to give an outer-sphere complex. The charge transfer transmitted towards the metallic center [29] leads to deprotonation of a coordinated ammonia molecule



$$H_3N \rightarrow \overset{NH_3}{\underset{NH_3}{Li}} \leftarrow \overset{H}{\underset{H}{N}} - H \leftarrow \overset{Ph}{\underset{Ph}{:C}} - H \rightleftharpoons Li^+NH_2^- + H - \overset{Ph}{\underset{Ph}{C}} - H$$

Coordination

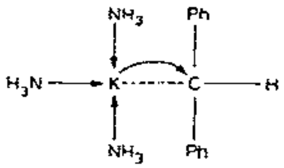
Induced effect

Outer-sphere coordination

Induced heterolysis

On the other hand the solvation enthalpy will be lower for the potassium compound and hence formation of the separated carbanion may not be possible. If the free carbanions were formed, the outer-sphere complexation would be expected to be weaker in the potassium compound, as the hydrogen atoms of ammonia molecules are less acidic, when coordinated to a potassium ion, as compared to that to a lithium ion.

It should be expected that the reactivities of the organoalkali—metal com-



pounds will be considerably changed in the presence of a crown ether, capable of specific and strong solvation of a certain alkali metal ion.

The formation of carbanions by deprotonation of an acid can also be considered as due to stabilization of the cationic species, namely the proton by coordination of a base B:

$$B + H{-}CR_3 \rightleftharpoons B{\rightarrow}H\cdots CR_3^- \rightleftharpoons BH^+ + CR_3^-$$

These effects have been extensively reviewed by Cram [47]; recent evidence supports the idea that the intermediate species, which is considered a contact ion pair should be more realistically considered as an unionized entity, as derived from conductivity measurements on quinuclidine hydrochloride and *n*-butylamine hydrochloride in a number of non-aqueous solvents [92]. In these compounds the hydrogen atom bonded to the nitrogen is sufficiently acidic to undergo hydrogen bonding interactions with either the chloride ion or the donor sites of the solvent molecules. Measurements in several solvents with similar dielectric constants clearly show that the extent of "ion pair" formation primarily depends on the donor and acceptor properties of the solvents.

$$R_3NH^+\cdots Cl^- + nS \rightleftharpoons [R_3NH\cdots S]^+ + [Cl(S)_{n-1}]^-$$

Dissociation of the "ion-pair" is favored by increasing donor number and increasing anion solvating properties of the solvents. In solvents with weak donor properties and low anion solvating power there is evidence for the formation of triple ions even in media with dielectric constants as large as ≈35. The triple ions probably contain a chloride ion acting as a bridging ligand between the acidic hydrogen atoms of two ammonium ions. The variation of the "dissociation" constants is understood as a function of the donor and acceptor properties of the solvents and their dielectric constants.

We have seen that increasing stability of the metal ion due to solvation permits for the alkyl group increasing perfection in approaching the carbanion structure. At the same time the Lewis acid strength and hence the reactivity of the metal ion is decreased by solvation. In a solvent of given donicity the Lewis acid strength of the cation is progressively lowered the greater the Lewis acid strength of the unsolvated cation. Polarographic evidence is available for the greater free enthalpy of solvation of the lithium ion as compared to that of the sodium and potassium ion [93] (Fig. 3).

In all reactions in which the lithium salt is less reactive than the corresponding sodium or potassium salts, the alkali metals are not attached to a carbon atom and the reactivity of the salt depends on the reactivity of the

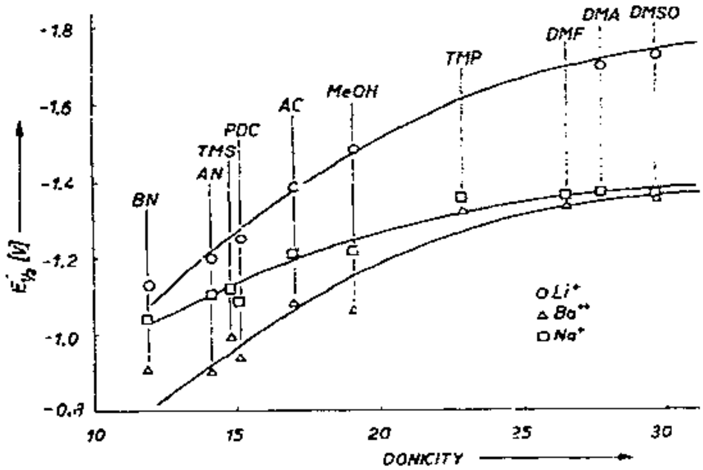


Fig. 3. Half wave potentials of Li^+, Na^+ and Ba^{++} in different solvents as function of solvent donicities.

metal ion. For example in the reaction of 2,6-dimethylphenoxide with alkyl halides [94] in ethyl ether it was found that under conditions which lead to about 55% reaction with the sodium salt, the lithium salt failed to react appreciably. The obvious interpretation is the stronger solvation of Li^+ by other molecules, which separates the lithium from the oxygen atom and prevents the lithium ion from nucleophilic attack by the halide atom of the alkyl halide.

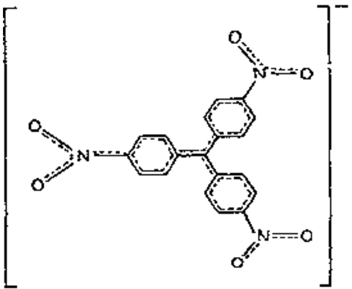
In an analogous manner the observed unreactivities of lithium salts can be explained, such as the hydrolysis of a number of esters [95,96] or the isomerization of oximes [97].

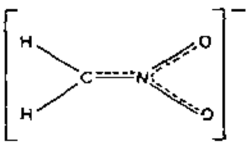
D. STABILIZATION OF ANIONS

Since the constitutional contributions to the stabilities of carbanions have been reviewed by Cram [47] we shall discuss merely the effects of the medium.

Stabilization of anions is effected by coordination of Lewis acids [30,31]. For example carbanions may be stabilized in hydrogen bonding solvents: the stronger the solvation of the anion by electrophilic solvent molecules the smaller is its reactivity (its basicity) and the higher its stability as compared to that of the unionized species.

The influence of anion solvation on the acidities of nitro-compounds can be seen from the comparison of the nitromethylamine and tri-*p*-nitrophenylmethylamine in DMSO and in protic media, such as water—alcohol [98]. DMSO is considerably weaker as an anion solvating agent than water—methanol mixtures (Table 2). Hence in the weakly anion solvating DMSO the tri-*p*-nitrophenylmethyl anion (I) is more stable than the nitromethylanion (II), as in (I) the negative charge is distributed over a considerably greater area than in (II).


(I)


(II)

Hydrogen bridging media (in general Lewis acids) interact more strongly with (II) than with (I) to give an improved charge distribution by strong solvation: the relative acidities of tri-*p*-nitrophenylmethane and nitrobenzene are reversed by replacing DMSO by a hydrogen bonding solvent or solvent mixture [47,99].

Potassium-*t*-butanolate is a weak deprotonating agent in *t*-butanol while in DMSO, a much weaker anion solvating agent, it acts as a considerably stronger base [47]. It has been shown, that there is a vast increase in kinetic activity of alkoxide anions in DMSO over that in hydroxylic solvents. The rate of isotopic exchange catalysed by potassium *t*-butoxide-0,9-M *t*-butylalcohol in DMSO is about 10^{13} times that observed in methanol—potassium methoxide. The *t*-butoxide anion is a still stronger base in the gas phase. The observed effects are related to the anion solvating effects of the medium: the greater the solvation (for example by a hydroxylic solvent) the smaller is its basicity.

The stabilization of inorganic anions is particularly important for the formation of unsolvated and hence highly reactive carbonium ions [100], which are required for the occurrence of cationic induced reactions. For example the ionization of triphenylchloromethane is drastically increased by the presence of Lewis acids. The ionization constant in a given solvent depends on the Lewis acidity of the EPA-molecules. It decreases in the order $SbCl_5 > SnCl_4 > ZnCl_2 > SbCl_3 > PCl_5$. The Lewis acidity is further decreased by increasing donicity of the solvent, as the actual reaction is represented as a ligand exchange reaction between solvent molecules S and Cl^- [101]:

$$Ph_3CCl + S.SbCl_5 \rightleftharpoons Ph_3C^+ + SbCl_6^- + S$$

TABLE 5

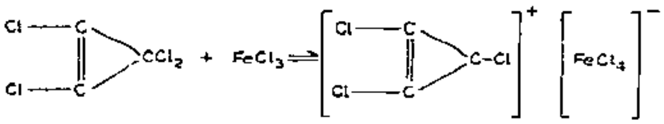
log $K_{[Ph_3C^+MCl_{n+1}]^-}$ values in acetonitrile (*DN* = 14.1) and in $PhPOCl_2$ (*DN* = 18.5)

Lewis acid	Complex anion	log *K* in AN	log *K* in $PhPOCl_2$
$SbCl_5$	$SbCl_6^-$	5.1	1.56
$SnCl_4$	$SnCl_5^-$	4.3	1.19
$ZnCl_2$	$ZnCl_3^-$	1.8	0.72
$SbCl_3$	$SbCl_4^-$	0.7	−1.60
PCl_5	PCl_6^-	0.5	−2.50

Likewise $t\text{-}C_4H_9F$ is ionized by electrophilic attack of fluorides [15,102].

$$t\text{-}C_4H_9F + AsF_5 \rightleftharpoons [t\text{-}C_4H_9]^+[AsF_6]^-$$

and chlorinated cyclic hydrocarbons by ferric chloride [103,104]

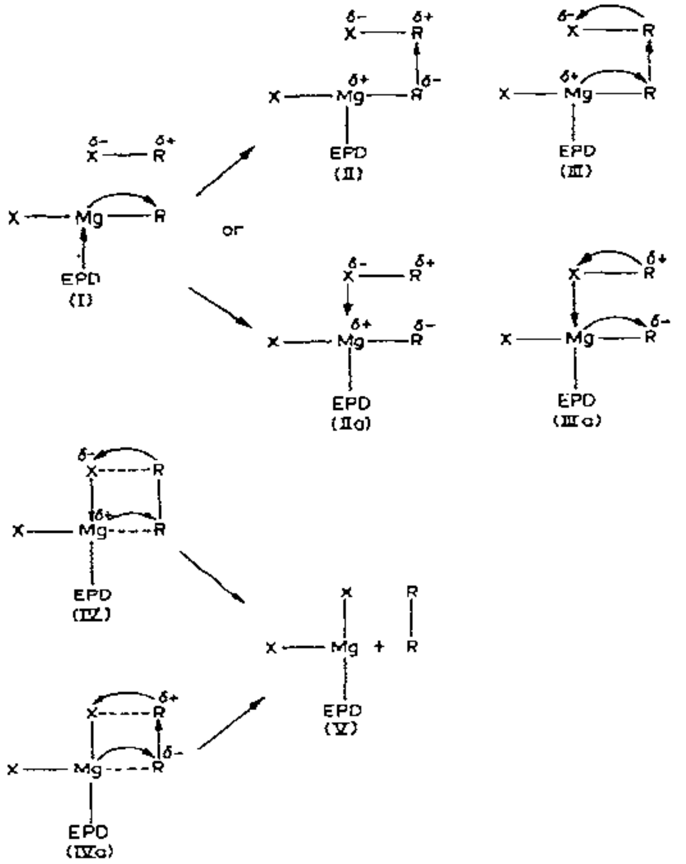


E. GRIGNARD REACTIONS

The prominent solvent properties of diethyl ether for Grignard reactions are well known. The elucidation of the crystal structure of the monomeric phenylmagnesium bromide dietherate [105] has established that two ether molecules are coordinated to a single magnesium atom. Dimethylmagnesium forms high molecular chains of alternating magnesium atoms and methyl groups [106] and in concentrated solutions of RMgX-species oligomeric species are present. In diethyl ether as a solvent they are coordinated by the solvent molecules [34].

The composition of the Grignard compounds in solutions is a function of the nature of the solvent, the nature of the R and X-groups as well as of the concentration. At concentrations below 0,1 M in diethyl ether monomeric species appear to be dominating and the mechanism of the addition of Grignard compounds to ketones has been presented in terms of an attack of monomeric or dimeric RMgX-species [107]. Various Grignard reactions have been interpreted in terms of attack of the dimeric species [108—111] but we shall assume for the present discussion of the electronic effects a mechanism involving monomeric alkylmagnesium halide species and a four-membered ring as a transition center. We shall assume further that the same mechanism should prevail in different solvents.

The coordination of the EPD-molecules to RMgX-species induces a polarization of the metal—carbon bonds (I), by which the negative fractional charges and hence the nucleophilic properties at the carbon atoms are in-



creased to such an extent, that interaction with the electron deficient alkyl groups of RX is taking place (II). This coordinating interaction induces further polarization of both the Mg—R and the R—X-bonds (III). The induced increase in Lewis acid properties at the magnesium atom and the induced increase in nucleophilic properties at X in the alkyl halide allow the electrophilic attack at the carbon atom in R—X (IV). In this way further polarization of both the Mg—R and the X—R-bonds is induced, to such an extent that heterolysis (V) can take place.

Alternatively the reaction may be initiated by the nucleophilic attack of X in RX at the magnesium (IIa) followed by the steps represented as (IIIa) and (IVa) to give finally (V).

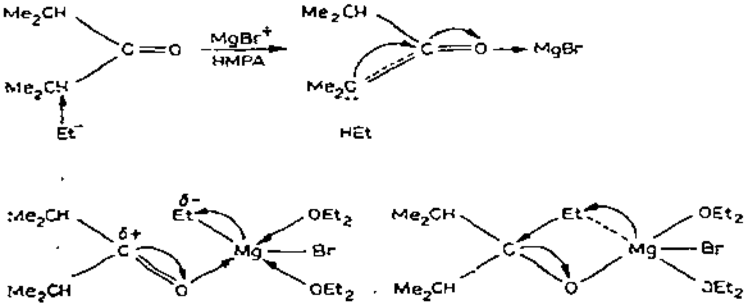
For this mechanism a suitable range in solvent donor properties is required. A weak nucleophile cannot initiate the reaction due to insufficient polarization of the Mg—R-bond. On the other hand, a very strong coordinating solvent such as HMPA (*DN* = 38,8) heterolyzes the Mg—R bonds due to stabilization of the cation by solvent coordination. The strong solvation decreases the electrophilic properties of the cation to such an extent that it cannot be active in step (IV). The decrease in reactivity of a metal ion by strong coordination is seen by the retardation of the addition of di-*n*-butylmagnesium to acetone if diethyl ether is replaced by the stronger solvating tetrahydrofuran [112]. Indeed, the solution of benzyl magnesium chloride in HMPA shows the red color characteristic for the carbanion [35]

$$C_6H_5CH_2MgCl + n\ \mathrm{HMPA} \rightleftharpoons [C_6H_5CH_2]^- + [(\mathrm{HMPA})_n MgCl]^+$$

$$C_6H_5CH_2MgCl + n\ \mathrm{HMPA} \rightleftharpoons [C_6H_5CH_2]^- + [(\mathrm{HMPA})_n Mg]^{2+} + Cl^-$$

A high solvent donicity not only reduces the electrophilic properties of the magnesium, but indirectly also increases the nucleophilic properties at R and this may occur to such an extent that the reaction takes an entirely different course. For example diisopropylketone reacts with ethyl magnesium bromide in HMPA to give the enolate [113]. The free carbanion deprotonates the ketone with formation of a diisopropylketone carbanion which is so strongly nucleophilic that it displaces HMPA from the coordination sphere of the $MgBr^+$-ion.

On the other hand in diethylether the tertiary carbinolate is formed [98]. Ethyl ether polarizes the Mg—C-bond to a considerably lesser extent and the coordination of magnesium to the carbonyl group induces a fractional positive charge to the C-atom of the C=O group (I). Coordination of the ethyl group to the electrophilic carbon atom leads to heterolysis of the Mg—C-bond (II).



(I) (II)

The unique usefulness of etheral solvents for Grignard reactions is not only due to their suitable donicities (Table 1) and lack of acceptor properties (Table 2) but also to the resistance of their bonds to polarization by interactions with the solutes. While most EPD-solvent molecules are enhanced in acidity due to coordination and to subsequent inductive effects, the ether molecules retain their molecular structure after coordination and remain strictly non-acidic. On the other hand, protonic solvents such as water or ethyl alcohol ($DN \approx 19$) cannot be used, since coordination produces such inductive effects leading to deprotonation (Zerevitvinov-reaction). The small enolization tendency of ethers and of HMPA seems to be related to their low EPA-properties.

Non-protonic solvents of medium donicity are acetonitrile (DN = 14.1), ethylenecarbonate (DN = 15.0), sulfolane (DN = 14.8) or PDC ($DN \approx 16$). As they contain C≡N, C=O or S=O groups respectively, which are readily coordinated to the magnesium with subsequent induced bond polarizations within the coordinating groups, the reactivities of the coordinated solvent molecules are changed appreciably. Hence the reactions take a different course.

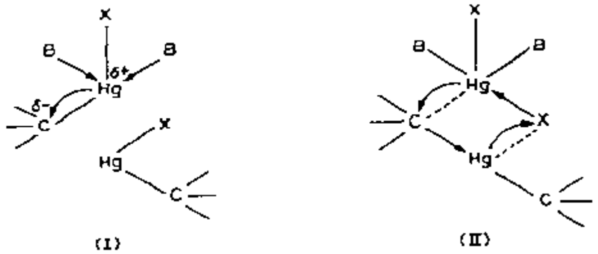
F. SUBSTITUTION REACTIONS INVOLVING ORGANOMERCURY COMPOUNDS

Reutov and Beletskaya [114] demonstrated that the mechanism of numerous organometallic reactions involve both nucleophilic and electrophilic actions of a solvent (or of a catalyst) and the reactant or vice versa. Apart from that, they emphasize that the nature of the substituents also exerts a strong influence on the reaction rates.

The symmetrization of ethyl-α-bromomercuriaryl salts

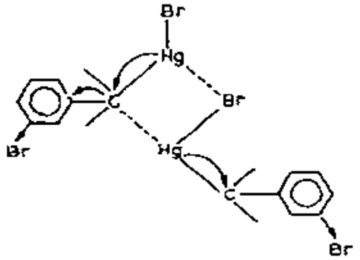
$$2\ RHgX \rightleftharpoons R_2Hg + HgX_2$$

occurs under the influence of Lewis bases, where the transition state is best represented as a four-membered ring, preceded by the formation of the complex between the base and the organomercury-compound. The nucleophilic attack of the base molecules at one or both mercury atoms induces the polarization of the adjacent Hg—C-bonds with corresponding increase in electrophilic properties at the mercury atoms (I). The coordinating interactions (II) lead to the formation of a four-membered ring with further polarizations of both the Hg—C and the Hg—X-bonds, which are finally heterolyzed.

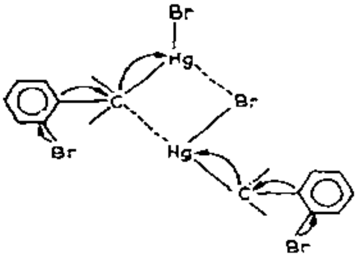


(I) (II)

Indeed the rupture of the Hg—C-bond plays the most important part in the reaction rate, which is slowed down as the ability of the substituent to supply electrons to the reaction center is increased. The reaction rates for bromine substituted mercurated esters decrease in the order *meta* > *para* > *ortho*. Thus bromine shows the greatest rate increasing effect when in the *meta* position where it can withdraw electrons from the reaction center by an inductive mechanism which leads to weakening of the old Hg—C-bond as well as to an increase in electrophilic properties of the mercury atom; the opposite effect is observed for bromine in the *ortho* position, where because of the conjugation with the benzene ring electrons are supplied towards the reaction centers



old C–Hg bond weakened, and electrophilic properties at Hg increased



old C–Hg bond strengthened, and electrophilic properties at Hg decreased

The effect of the nature of the halogen atom on the reaction rate cannot be explained on the basis of the inductive effects alone, unless the phenomenon of coordination selectivity is taken into account [99] as iodine has the greatest and fluorine the smallest effect on the rate. This is in agreement with the high stability of the mercury—iodine bond. The effect of certain solvents has been studied for the electrophilic reaction of benzylmercury chloride with iodine and in order to avoid symmetrization in the presence of a tenfold excess of cadmium iodide [114]

$$C_6H_5CH_2HgX + I_2 \rightarrow C_6H_5CH_2I + HgXI$$

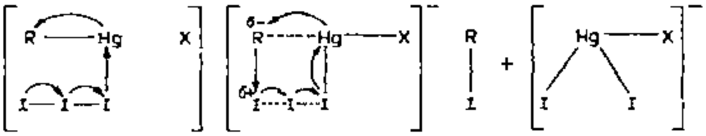
TABLE 6

Influence of the solvent on the reaction of benzylmercury chloride with iodine in the presence of iodide ions

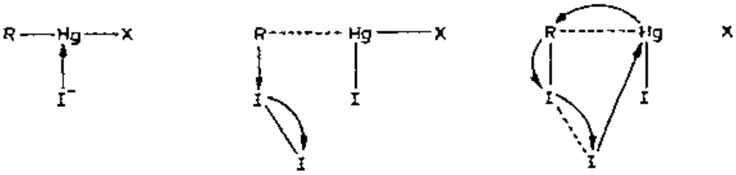
Solvent	ϵ	*DN*	$k_2(20°)$ [l mol^{-1} sec^{-1}]
Methanol	35.2	19	0.807
Acetonitrile	37.5	14	0.590
70% aq. Dioxan	18.0	?	0.366
Ethanol	24.8	18.5	0.279
DMF	36.5	27	0.215
DMSO	48.9	30	0.145
Butanol	19.0	18	0.072

The reaction was shown to proceed in all solvents investigated (Table 6) by the same mechanism and consequently through the same transition state. With an excess of iodide ions practically all of the iodine present in the solution is complexed and the nature of the cation has little effect on the rate of the process. It has been established that the electrophilic substitution occurs under the action of the triiodide ion. It has been proposed that the interaction between benzylmercury chloride and the triiodide ion begins with a nucleophilic attack by the triiodide ion at the mercury atom. This coordination induces a polarization of both the C—Hg- and the I—I-bonds (I), which provides an increased nucleophilicity at the C-atom and an increased electrophilicity at the terminal iodine atom. As a result a coordinate link is formed and further bond polarizations induced in this transition state. A five-membered ring has been suggested as a possibility for its geometry (II), in which both the C—Hg- and the I—I-bonds are more strongly polarized and the Hg—I-bond less polarized than in (I); hence the former bonds are heterolyzed (II) with simultaneous formation of a further Hg—I-bond [114].

Another possibility which has been discussed is that the first step is the formation of a complex between the organomercury compound and iodide ion (Ia) with subsequent electrophilic attack of the carbon atom by an iodine molecule (IIa) and final heterolysis of the C—Hg and I—I-bonds (IIIa).



(I) (II) (III)



(Ia) (IIa) (IIIa)

The choice between the two mechanisms is difficult, especially as the transition states in both cases differ only in degree of bonding between iodide ions and iodine and hence the electronic interpretation remains in principle the same in both cases.

The reaction is considerably faster in benzene solution than in any other solvent under consideration [114]. Addition of a donor solvent leads to a lowering of the reaction rate. It is obvious from Table 6 that the reaction rate is not a function of the dielectric constant of the medium.

The role of the electrophilic solvent properties may be judged from the comparison of the actions of the aliphatic alcohols. Their donicities are similar, while their electrophilic properties decrease considerably in the series MeOH > EtOH > PrOH > BuOH (see Table 2). In this way there is a corresponding decrease in anion solvation and hence an increase in nucleophilic properties of the triiodide ions. Decrease in electrophilic properties of the alcohol molecules causes the same effect as addition of iodide ions to the system, an effect which is not fully understood in terms of the suggested mechanisms.

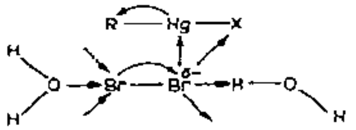
The available experimental evidence is unsufficient to account for the influence of the nucleophilic solvent properties. Due to the coordination selectivity of metal ions [115—117] the donicity concept cannot be expected to be applicable as soon as soft metal ions are compared in their behaviour towards hard ligands (solvent molecules) and soft ligands (iodide) [118]. From the proposed reaction mechanism one would expect that increasing solvation of the mercury atom due to nucleophilic attack by solvent molecules would lead to a decrease in its coordinating properties. If it is accepted, that the donor properties of AN towards Hg^{2+} are greater than would be suggested by its donicity (strong coordinating interactions have been observed between AN and Ag^+ [119]), a reasonable relation is found of decreasing reaction rates by increase in aprotic solvent donicities towards Hg^{2+} (Table 6). The differences in electrophilic properties for the solvents AN, DMF and DMSO are not vast. One would expect a particularly low reaction rate in HMPA, where its high *DN* as well as the extremely low anion solvating (electrophilic) properties are expected to operate in the same direction.

The cooperative nucleophilic and electrophilic solvent effects appear to operate in opposite directions for the reaction

$$-C-HgCl + Br_2 \rightarrow -C-Br + HgClBr$$

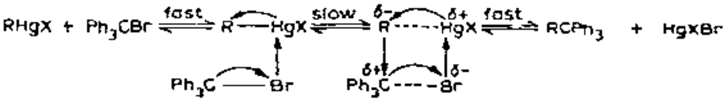
the rate of which is decreased by a decrease both in EPD- and EPA-solvent properties.

The influence of the additives is regarded as the phenomenon of nucleophilic catalysis leading to polarization of the bond within the bromine molecule. This process is further supported by electrophilic attack at the other end of the bromine molecule. This "push-pull"-effect is particularly strong for water and the pronounced effect of water would not be accounted for by the exclusive consideration of the differences in donor properties [114].

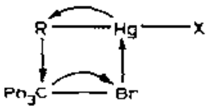


The formation of the coordinate Br—Hg link leads to further polarization of the Br—Br-bond and hence to an enhancement of the electrophilic properties of bromine towards the nucleophilic carbon atom.

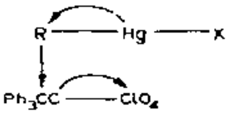
Another example for the occurrence of combined coordinating and inductive effects is the reaction of ethoxycarbonylbenzylmercury bromide and triphenylbromomethane. The intermediate formation of the 1 : 1 complex is due to nucleophilic coordination preceeding the electrophilic attack on the carbon:



The necessity of nucleophilic coordination at the Hg-atom for the occurrence of the electrophilic substitution has been termed "nucleophilic assistance". It is shown by the absence of an interaction of triphenylmethylperchlorate or with the corresponding halostannate. These anions are very poor electron pair donors and cannot be coordinated to the mercury atom and hence the electron dynamics of the reaction is not initiated. It can be proposed that the transition state with a closed structure (a) is energetically more convenient than the open structure (b) [114]:

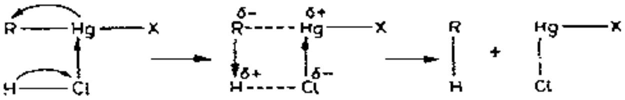


(a)



(b)

An analogous phenomenon is observed for the acid cleavage of RHgX under mild conditions. This is readily accomplished by hydrogen halides, while perchloric acid remains unreactive [114].



The reaction rate is decreased by increasing the water content which ionizes the hydrogen halide to give stable ionic species.

G. CONCLUSION

A unified approach is presented for the understanding of solvent effects in organometallic reactions. The description is based on very simple rules in coordination chemistry. Solute—solvent interactions are considered to lead to induced changes in bond properties and hence in nucleophilic and electrophilic properties of the solute. By the use of empirical parameters namely the donicity (expressing the solvent basicity) and the acceptor number (representing the Lewis acidity) and understanding is gained of the effects exerted either by different solvents or by different metal ions. It is shown that

(1) the concept of contact-ion pairs is no longer needed,

(2) the reactivity of carbanions is increased by increased stability of the counter ion,

(3) the reactivity of carbanions is decreased by increased solvation with electrophiles,

(4) the reactivity of carbonium ions is enhanced by increasing stability of the anion,

(5) in most cases the ionic state of the intermediates is not reached, as the nucleophilic or electrophilic changes due to solvent coordination are suitable for the interaction to proceed,

(6) ethers are ideal solvents for Grignard reactions due to their pronounced donor properties, the absence of electrophilic character and the reluctance to undergo induced bond polarizations due to coordination.

It is hoped that the views presented will initiate more systematic research on solvent effects for different types of organometallic reactions, which may in turn provide a more quantitative pattern.

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