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THE EFFECT OF SOLVENT UPON THE RATES AND MECHANISMS OF ORGANOMETALLIC REACTIONS.

I. GENERAL ASPECTS

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SUMMARY

The data reported to date on the effect of solvent upon the rates and mechanisms of organometallic reactions have been analysed and discussed and indicate that the effect is very complex. The analysis also shows that there is no overall explanation for the effect and that indeed such an explanation seems at present to be non-existent.

It is suggested that the problem may be successfully approached through a study of the effect of the solvent upon the redistribution of organic groups between organometallic molecules. In these reactions, not only the kinetics of the reactions in various solvents should be studied but also identification of the organometallic complexes is essential as well as the electronic structures and geometries of the complexes in the crystalline phase and in solution.

INTRODUCTION

The effect of solvent upon the reactivity of organometallic compounds is one of the most important unsolved problems in organometallic chemistry. Although the effect is long established, we are still a long way from rationalising, let alone predicting, the effects which have been observed. This may be attributed to the difficulty of the problem on the one hand, while on the other thorough quantitative studies in the field are not numerous.

This is the first in a series of papers devoted to an experimental study of the effect of solvent upon the structures and reactivities of organometallic compounds. Initially, we believe it necessary to analyse the experimental data reported to date and to discuss ways in which the problem could be investigated and resolved.

DISCUSSION

As early as 1929–1930, Ziegler and co-workers[1,2] showed that organolithium compounds in diethyl ether (DEE) were much more reactive than in hydrocarbons. Thus, addition of alkyllithium compounds to 1,1-diphenylethylene increased sharply when benzene was replaced by DEE[1] as the solvent. Later, Waack and co-workers showed[3] that the reaction was practically instantaneous in tetrahydrofuran (THF). n-Butyl bromide reacts with n-butyllithium 20 times faster in DEE compared with benzene[2] while the same reaction was 10,000 times slower in n-hexane than in the presence of equimolar (with respect to n-butyllithium) amounts of DEE[4]. n-Butyllithium reacts with 1-bromooctane 1000 times faster in DEE than in n-hexane[5].

In reactions of this type, it has been found that the solvent often influences not only the rate but also the mechanism of the reaction. Thus, n-butyllithium reacts with benzyl chloride in n-hexane to give bibenzyl and n-pentylbenzene[6], which may be explained by assuming that the benzyllithium formed as an intermediate reacts with additional benzyl chloride as well as with n-butyllithium. When the reaction was carried out in THF, in addition to the usual products, a 28% yield of trans-stilbene and smaller amounts of n-butylbibenzyl were also observed, whose presence was attributed to the formation of α-chlorobenzyllithium which then reacted further to give α-chlorobibenzyl which, in turn, reacted with butyllithium.

The effect of the solvent upon the reactivity of alkyllithium compounds was also observed during the metallation of hydrocarbons. Gilman and co-workers[7,8] showed that the metallation of dibenzofuran, dibenzothiophene and *N*-ethylcarbazole was accelerated strongly by the following series of solvents: n-hexane < DEE < THF. The use of amino solvents had an even greater effect. Thus the complex of butyllithium with *N,N,N′,N′*-tetramethylethylenediamine, in contrast to the corresponding solution of butyllithium in n-hexane, readily metallated toluene and even benzene[9].

So the increased reactivity of organolithium compounds in electron-donor solvents has been reliably demonstrated for the Würtz reaction and for addition and metallation. Eastham and Gibson[5] have concluded that the increase in reactivity might be explained by assuming that the effective association of the organolithium compounds decreases and the charge separation increases in transition state when hydrocarbons are replaced by electron-donor solvents. Later, Screttas and Eastham[10] suggested that electron-donor solvents when added to solutions of alkyllithium compounds in hydrocarbons influence the reactivity to different extents depending on whether the ratio $r = [D]/[RLi]$ is less or greater than 0.5. When $r < 0.5$, electron-donor solvents are thought[10] to solvate less reactive associates thus enabling these to dissociate further to give more reactive dimers.

$$(Bu_2Li_2)_3 + 3\,THF \rightleftarrows 3\,Bu_2Li_2 \cdot THF \tag{1}$$

When $r > 0.5$, the solvent might facilitate charge transfer from the alkyllithium compound to the substrate Z and thus accelerate the reaction.

$$Bu_2Li_2 \cdot THF + \text{solvent} + Z \longrightarrow (Bu_2Li_2 \cdot THF)^{+}_{\text{solv}} + (Z)^{-}_{\text{solv}} \tag{2}$$

Kovrizhnykh and Shatenshtein[11] support this viewpoint but in addition suggest that acceleration at $r > 0.5$ may be explained by an additional solvation of lithium associates followed by the formation of an admittedly small number of more reactive alkyllithium complexes with the Lewis base. Brown[12,13] disagrees with Waack *et al.*[3,14] who believe that only the monomer B is reactive in the Ebel[15] scheme which provides a description of how the nature of the C–M bond varies as a function of the solvent, metal and R.

$$\underbrace{(RM)_6 \rightleftarrows (RM)_4 \rightleftarrows (RM)_2}_{A} \rightleftarrows \underset{(B)}{RM} \rightleftarrows \underset{(C)}{R^-M^+} \rightleftarrows \underset{(D)}{R^-\|M^+} \rightleftarrows \underset{(E)}{R^- + M^+} \tag{3}$$

Brown has assumed that solvated dimers $(RM)_2$ or even free carbanions (if the solvent is strongly solvating) may participate in the reaction. The fact that the monomer and dimer species may react simultaneously has been subsequently verified[16] but despite extensive studies[14,16] no evidence was obtained for the existence of carbanions in the system.

The above detailed discussion of the effect of the solvent upon organolithium reactivity may be explained by the fact that the most notable achievements to date have occurred entirely in this field whereas with other organometallics both experimental data and attempted explanations are rather contradictory.

The situation with organomagnesium compounds is typical. Normant[17] has shown that halogenated acetylenes do not react with Grignard reactants in DEE or THF while they do so in HMPT. Zakharkin and co-workers[18] demonstrated that the yield of the "normal" Würtz reaction products increased considerably when alkylmagnesium halides reacted with alkyl halides in DME rather than in DEE.

$$RMgX+R'X \rightarrow RR'+MgX_2 \tag{4}$$

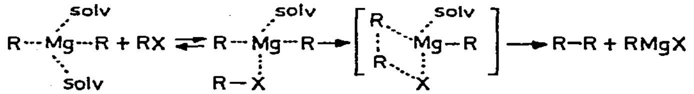
The accelerating effect of electron-donor solvents was also demonstrated in reactions involving exchange of R for R' groups[19],

$$RMgX+R'X \rightarrow R'MgX+RX \tag{5}$$

and in other metallations of hydrocarbons with alkylmagnesium halides[20].

It was shown[21] that organomagnesium compounds in strongly solvating solvents could alkylate element–halogen bonds as readily as organolithium compounds.

These qualitative data led Okhlobystin[22] to the conclusion that the use of strong solvating solvents in nucleophilic substitutions involving organomagnesium compounds strongly accelerates the corresponding reactions. As early as 1963, however, Becker showed[23] that Grignard reactants interact with nitriles in solvating solvents at a slower rate than in neutral solvents. A similar effect was found for reactions or organomagnesium compounds with ketones[24–26], 1-alkynes[27] and β,γ-unsaturated esters of 2,4,6-trimethylbenzoic acid[28]. Witt and Khristova[29] have applied gas–liquid chromatography to a study of the effect of solvent and Grignard reactant concentration upon the rate of the reaction of 2-hexylmagnesium bromide or chloride, 1-hexylmagnesium chloride, or 2-butylmagnesium chloride with the respective alkyl halides in DEE or THF. The rates at which diastereomeric products of the Würtz reaction were formed were shown to be independent of the concentration of the reactants. The yield decreased when DEE was replaced by THF. Small amounts of HMPT added to the reaction mixture did not affect the rate. The following mechanism was assumed[29] for the Würtz reaction.



(6)

The reactions with DEE and THF as solvents were suggested as involving polarisation (with no carbanions being formed) while the reaction in HMPT involved ionisation (and the formation of carbanions).

Wakefield[30] has suggested three mechanisms which could describe the effect of the solvent upon the reactivity of Grignard compounds:

(*i*). Spatial effects, due to coordination involving the solvent in the transition state, upon the direction of the reaction.

(*ii*). The effect upon the strength and reactivity of the C–Mg bonds and upon the concentration of the active species.

(*iii*). The effect on the ease of formation of the Grignard reactant.

Using Dessy and Paulik's approach[31] to this problem, Wakefield has concluded that the coordination of the solvent with the Grignard reactant may increase the lability of both the Mg–C and Mg–X bonds; this may increase the tendency of the carbon atom to be involved in carbanion formation and at the same time favour the formation of solvated RMg^+ ions which are more reactive (both electrophilically and nucleophilically) in comparison with the undissociated molecules. The RMg^+ reactivity will, however, fall as the solvating power of the solvent increases. The use of such a model allows a complete qualitative explanation of the available experimental evidence, but unfortunately it allows no further predictions which somewhat limits its application.

In order to solve the above problem it would appear that systematic data on the effect of the solvent upon rates and mechanisms of the reactions involving organomercury compounds would be especially interesting in view of the fact that studies of these compounds have enabled the main mechanistic regularities to be clarified for organometallic compounds[32]. To date, however, experimental data on these compounds are scarce and what is available is rather controversial.

In 1959, Ingold and co-workers showed[33] that di-sec-butyl mercury dismutates with mercury dibromide in ethanol five to six times slower than in acetone. In the same year, Dessy and co-workers found[34] that symmetrical organomercurials were protodemercurated with halogen hydrides in DMSO at a slower rate after dioxane or water had been added to the solution.

In 1961, it was shown in our laboratory[35] that both the kinetic order and the mechanism of the reaction varied when isotopic exchange of $C_6H_5CH(HgBr)COOC_2H_5$ with Hg^*Br_2 was carried out in 70% aqueous dioxane rather than in pyridine. The overall order was two (unity with respect to each of the two components), with respective values of $k_2 = 6.6 \times 10^{-2}\ l \cdot mol^{-1} \cdot s^{-1}$ at 60°C, $E_a = 16.3\ kcal \cdot mol^{-1}$ and $\Delta S = -15.5\ cal \cdot mol^{-1} \cdot K^{-1}$ in pyridine, whereas in 70% aqueous dioxane the order was unity with respect to the organomercury compound and zero with respect to Hg^*Br_2, $k_1 = 5.6 \times 10^{-4}\ s^{-1}$ at 60°, $E_a = 26.7\ kcal \cdot mol^{-1}$ and $\Delta S = +4.6\ cal \cdot mol^{-1} \cdot K^{-1}$. These facts demonstrate that the reaction is strongly decelerated when pyridine is replaced by 70% aqueous dioxane and that the S_E2 mechanism is changed to S_E1.

Subsequent to this study, solvent-induced alterations of the kinetics and mechanism have been observed for organomercury compounds during isotopic exchange of benzyl-[36] or phenylmercury halides[37] with Hg^*Br_2, in the dismutation of symmetrical organomercurials in the presence of mercury halides[38,39], in halodemetallation of vinyl[40], phenyl[41], or benzyl[42] derivatives of mercury, in protodemetallation of phenylmercury bromide[43], 2-chlorovinylmercury chloride[44], or benzylmercury chloride[45], and in alkylations of organomercury compounds[46,47].

In interpreting their data, Dessy and co-workers[38] noted that the activation energy of dismutation of diphenylmercury with mercury di-iodide increases when cyclohexane and benzene are replaced by ethanol and dioxane as solvents, and attributed this to the solvation of the organomercurials in their ground states, the solvation leading to an increase in the ground-state energy. For strongly solvating solvents, greater variations in the entropy of activation should be observed[38]. In our laboratory it was shown that the effect of the solvent upon the energy parameters might be in opposite directions for different types of organomercury reactions. Thus, in the isotopic exchange of mercurated phenylacetates with Hg^*Br_2 in aprotic solvents (pyridine, DMF, DMSO), the energies and entropies of activation are lower than in protic solvents such as aqueous dioxane or aqueous ethanol[48]. In contrast, the energies and entropies found for the reaction of benzylmercury chloride with iodine in protic solvents are lower than those in aprotic solvents[42].

Consequently, the effect of the solvent upon the behaviour of organomercury compounds as with organomagnesium compounds, is very capricious and any explanation of the effect demands the use of a multilateral approach. Such an approach will be discussed below.

The redistribution of organic groups in organoaluminium compounds has revealed a much clearer picture of the solvent effect. It has been shown that exchange between Me_3Al and Ph_3Al is complete in 1 min in DEE or THF as the solvent[49] whereas 1 day is required in pyridine or lutidine[50]. Mole and co-workers[51] used NMR spectrosocopy to show that the exchange between etherates of Me_3Al and Me_2EtAl or between etherates of Me_2AlCl and Me_2AlBr does not involve preliminary dissociation of the etherates whereas exchange between the anisole complexes of Me_2PhAl and Me_3Al proceeds after only one of the complexes has dissociated (this was not a rate-controlling step). Mole[52] concluded that solvation of organoaluminium compounds reduced their reactivity in organic group redistribution reactions.

On the other hand, it is known that alkylaluminium compounds alkylate element–carbon bonds much more readily when they are complexed with ethers or amines[53,54]. Also, it has been shown[55] that complexes of the type $R_3Al \cdot R_3N$ metallate acetylene homologues whereas trialkylaluminium compounds are themselves involved in addition at the triple bond[56].

With organotin compounds, the solvent effect has been extensively studied by Nasielski[57] and co-workers for the halodestannylation of various organotin derivatives. A rule has been suggested that the reactivity of tetra-alkyltin compounds is due to spatial effects ($Me > Et > Pr > i\text{-}Pr$) when the reaction is carried out in polar solvents (CH_3OH, DMF, CH_3COOH, DMSO), and to induction effects ($Me < Et > Pr < i\text{-}Pr$) in non-polar solvents (C_6H_5Cl, CCl_4, cyclohexane). The authors[57] believe that in polar media the solvent acts as a nucleophilic catalyst, forming a complex with the organotin compound, the complex subsequently reacting with the halogen to yield the reaction products. In non-polar solvents, Eaborn and co-workers[58] have shown that two halogen molecules are involved in the rate-controlling step, one of them acting as a nucleophilic catalyst and the other as an electrophile.

In this short review it is not possible to discuss all the various studies pertaining directly or indirectly to the influence of the solvent upon organometallic reactivity; however, the discussion given above demonstrates that the effect is very complex and depends on the nature of the organometallic molecule and substrate as well as on the type of reaction involved. At the present moment, therefore, it is not possible to accurately answer the question "How does a given solvent influence the reactivity of a given organometallic compound?". Various attempts have been made by some authors, however, but these are at best of limited significance. Thus, Rochow, Hurd and Lewis[59] in their book "The Chemistry of Organometallic Compounds" have stated that solvation of an organometallic molecule is accompanied by transfer of electrons from a donor atom in the solvent, leading to a decrease in the carbon–metal bond polarity and hence to decreased reactivity of the organometallic compound. The same point of view is supported by Pauson[60] who believes that all organometallic compounds become less reactive after they have been complexed; Pauson emphasises that the greater the donor activity of the solvent the more pronounced the decrease in the organometallic reactivity. Okhlobystin[22] has expressed quite the contrary opinion. He assumes that complex formation leads to an increase in the carbon–metal bond polarity and hence to an increase in the rate of heterolytical substitutions and exchanges. It has been noted already that neither of these viewpoints may serve as a general rule since each approach explains only a particular set of data obtained for particular reactions of some organometallic compounds.

We believe that the effect of the solvent upon the rates and mechanisms of various organometallic reactions cannot be explained simply in terms of the variation in reactivities of organometallic molecules; other factors such as the effect of the solvent upon the reactivity of the second reactant or upon the solvation of the transition state are equally significant. The importance of the effect of the solvent on the reactivity of the reagent which attacks an organometallic molecule is very well illustrated by the data obtained by Pilloni and Tagliavini[61], who found that tetraalkyllead derivatives react with iodine 15 to 20 times faster in benzene than in CCl_4. Both benzene and CCl_4 are non-polar ($\mu=0$), have equal dielectric permeabilities ($\varepsilon=2.25$) and are equally ineffective at solvating R_4Pb molecules; however, they polarise iodine to different extents (benzene being much more effective than CCl_4, due to the formation of a charge-transfer complex[62]). On this basis, the observed difference between the reaction rates is easily explained. A similar analysis for solvents which both strongly solvate R_4Pb molecules and strongly polarise iodine molecules would be much more difficult since the series which govern the stabilities of the complexes might be different.

A similar approach may be applied to the analysis of the effect of the solvent upon the rates and mechanisms of the protodemetallation of organometallic compounds[34,43–45] and of other reactions. In our view, what is now needed is the most active attention to the effect of the solvent upon the redistribution of organic groups between similar organometallic compounds, in which the effect of the solvent upon the reactivities would be identical not only in its magnitude but also in its direction.

We are at present thoroughly studying the effect of the solvent upon the rates and mechanisms of organo-mercury, -platinum and -tin compounds. The main areas of investigation are the kinetics of the reactions in various solvents[63], the identification of molecular complexes involving organometallic compounds[64] and a study of the electronic structure and the geometry of the complexes both in the crystalline phase[65,66] and in solution[67,68].

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