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Kinetics and mechanism of the C-S coupling reactions of aryl Grignard reagents with aryl arenesulfonates

Research Article

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Abstract: The kinetics of the C–S coupling of arylmagnesium bromides with phenyl tosylate has been studied in THF: toluene at 90°C. The reaction is first order in Grignard reagent and first order in phenyl tosylate. Kinetic data, Hammett relationship and activation parameters are consistent with a nucleophilic addition mechanism involving rate determining attack of carbanion to sulfonyl group followed by a fast phenoxide group leaving.

Keywords: *Grignard reagents • Aryl carbanions • C-S coupling • Hammett plot • Activation parameters*

1. Introduction

Sulfones [1] are of great use in organic synthesis as useful intermediates, in medicine as important drugs, [2,3] and also in industry [4]. The use of sulfones in organic synthesis has increased significantly in the past twenty years and they have been employed for the synthesis of many functionalized compounds and naturally occuring products [5,6].

Sulfones can be synthesized by a variety of methods [1,7]. However, the use of organometallic methods are quite limited and they generally depend on the sulfonylation of carbanions with sulfonyl chlorides [8-10]. The use of sulfonates as partners in C-S coupling of organometallic reagents are rare (Scheme 1, path a). Organolithiums [11] and Grignard reagents [12,13] have been reported to react with arenesulfonates by S-O bond cleavage leading to the formation of sulfones.

However, sulfonates are well known as partners like halides in C-C coupling reactions of organometallic reagents, which are conceptionally among the most straightforward processes for forming C-C bonds [14]. Uncatalyzed or transition metal catalyzed reactions of organolithium, Grignard and organozinc reagents with sulfonates have been extensively studied. Copper catalyzed organolithiums [15], organocuprates [16-18]; or copper, nickel or palladium catalyzed Grignard reagents [16,19-22] and nickel or palladium catalyzed organozinc reagents [23,24] react with alkyl esters of alkane– and arenesulfonates by C–O bond cleavage leading to C-C coupling products (path b).

Recently, Grignard reagents have been reported to react with neopentyl arenesulfonates under nickel catalysis to yield C-C coupling products by C-S bond cleavage (path c) [25-27]. These findings show that in the reactions of sulfonates, either sulfonate groups (path b) or under nickel catalysis, neopentyloxysulfonyl groups (path c) can act as chemoselective leaving groups for C-C coupling. For C-S coupling, organyloxy groups are leaving groups (path a).

Sulfonyl chlorides also have ambident character. Grignard reagents and organozincs are known to give sulfones in their reactions with sulfonyl chlorides while organozincs generate C-C coupling products under Pd catalyzed conditions [28].

We have already investigated the reaction of aryllithium, -magnesium and -zinc reagents with arenesulfonates to develop a new route for the preparation of arylsulfones. We observed selective

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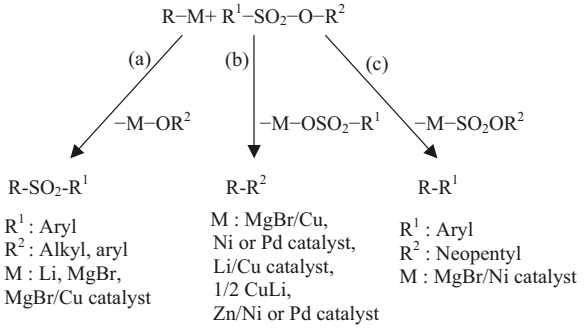


Scheme 1. Reactions of organometallic reagents with sulfonates. (a) C-S coupling reaction. (b) and (c) C-C coupling reactions.

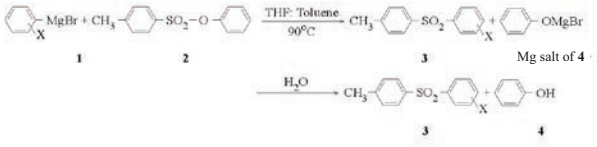
formation of C-C and C-S coupling products in the reaction of phenyllithium with 2-chloroethyl tosylate depending on the type of Cu(I) catalyst [29]. In uncatalyzed and Cu (I) catalyzed reactions of aryl Grignard reagents with phenyl tosylate, we found [30] that, aryl Grignard reagents **1** attack tosylate **2** only by S-O bond cleavage to give sulfones **3** (Scheme 2).

Our interest in the thiophilic reactivity of aryl magnesium bromides in their reaction with aryl arenesulfonates prompted us to find kinetic support for the sulfonyl transfer to Grignard reagents and to obtain information concerning the reaction mechanism. To the best of our knowledge, there is no reported work on the kinetics and mechanism of the reaction of Grignard reagents with sulfonates at sulfur center, although numerous studies have been reported on the kinetics and mechanism of the reactions of nitrogen and oxygen nucleophiles with sulfonates [31-36].

In this paper, we report our results in the kinetics and mechanism of the C-S coupling of Grignard reagent derived aryl carbanions with phenyl tosylate.

2. Experimental Procedures

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe-rubber septum techniques [37]. THF was distilled from sodium benzophenone dianion and toluene was distilled over sodium. The magnesium generally used was more than 99.9% pure. Commercially available bromobenzene and subtituted bromobenzenes were purified using literature procedures. Phenyl tosylate was prepared according to the published procedure and authentic sample of phenyl p-tolyl sulfone was prepared by our reported sulfone synthesis procedure [30] using phenyl magnesium bromide-phenyl tosylate coupling. Grignard reagent was prepared in THF by standard method and their concentrations were found by titration prior to use [38]. Thermo-Focus gas chromatograph



Scheme 2. Reaction of aryl Grignard reagents with phenyl tosylate to give sulfones.

equipped with a ZB-1 capillary column (immobilized with phenyl polydimethylsiloxane) and a flame ionization detector was used for GLC analysis.

The kinetics were followed by measuring the concentration of remaining phenyl tosylate and also concentrations of formed sulfone and phenol by GLC analysis using internal standard technique. In a jacketed two necked reaction vessel of approximately 25 ml capacity equipped with a reflux condenser and a magnetic stirrer, phenyl tosylate, toluene and internal standard was thermostatted at 90°C. THF solution of Grignard reagent was added rapidly to initiate the reaction. Aliquots (7-11) were withdrawn from the homogeneous solution at 15 minute intervals by syringe and were added to a vial containing a quenching solution of aqueous NH_4Cl solution for hydrolysis and ether.The vial was capped and shaken. Extraction of the remaining phenyl tosylate and products sulfone and phenol to the ethereal phase was found to be essentially quantitative. The ethereal phase was analyzed by GLC. Generally, self consistent data could be obtained for 2 or 3 half lives. Reproducibility of the rate constants was generally ±4%.

3. Results

For the kinetic study, the model reaction of phenylmagnesium bromide (X=Y:H, **1a)** with phenyl tosylate (**2)** was carried out in THF: toluene (7:10) at 90°C (Scheme 2). The rate data were collected by taking at least 7-11 samples at 10-15 minutes intervals and measuring the concentrations of phenyl tosylate (**2**), sulfone (**3a)** and phenol (**4)** in each sample by GLC analysis.

Since phenyl tosylate **2** reacts with phenylmagnesium bromide (**1a)** to give only C-S coupling we expected to find the same rate for the disappearance of sulfonate (**2)** and appearance of sulfone (**3a)**. In addition, the observed amounts of sulfone (**3a)** and phenol (**4)** versus time are expected to be equal. So, in the evaluation of rate data, we used directly measured and also calculated values for $c=[PhOTos]]_t$ *i.e.* the concentration of phenyl tosylate (**2)** at time t. As tosylate (**2)** reacts by giving only sulfone (**3a)** and phenol (**4)**, then c can also be calculated as $c=[PhOTos]_o - [PhTos]_t$ and$c = [PhOTos]_o - [PhOH]_t$,

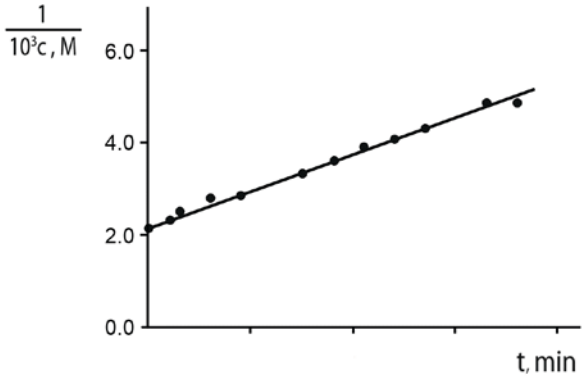


Figure 1. Typical second order plot for the reaction of phenyl magnesium bromide (**1a**) with phenyl tosylate (**2**) in THF: toluene (7:10) at 90oC; c= $[PhOTos]_t$. $[PhMgBr] = [PhOTos] = 0.471$ M.

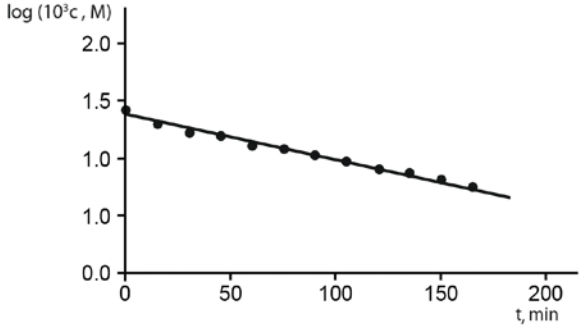


Figure 2. Typical first order plot for the reaction of phenylmagnesium bromide (**1a**) with phenyl tosylate (**2**) in THF: toluene (7:10) at 90°C; c= $[PhOTos]_t$. $[PhMgBr] = 0.560$ M, $[PhOTos] = 0.026$ M.

where $[PhOTos]_o$ shows the initial concentration of phenyl tosylate and $[PhTos]_t$ and $[PhOH]_t$ are the concentrations of products at time t, respectively.

We expected that direct and indirect calculation of $[PhOTos]_t$ values would give the same result in the evaluation of rate data for the reaction of Grignard reagents with phenyl tosylate leading to only formation of C-S coupling. We used two kinetic conditions: (a) nearly equal concentrations of phenylmagnesium bromide (**1a)** and phenyl tosylate (**2)** to find the total reaction order; (b) the variable concentration of phenylmagnesium bromide (**1a)** in excess and varied to find the reaction order in phenyl tosylate **2** and phenylmagnesium bromide (**1a)**.

(a) The first set of experiments were carried out using 0.471 M **(1a)** and 0.471 M **(2)** in THF toluene (7:10) at 90°C. We found that equimolar amounts of sulfone (**3a)** and phenol (**4)** were formed in the reactions and evaluated the rate data as total second order. We plotted (i) $1/[PhOTos]_t$ and (ii) $1/ ([PhoTos]_o - [PhTos]_t)$ and also (iii) $1/([PhOTos]_o – [PhOH]_t)$ values versus time. The plots proved linear up to 50-80% completion of the reaction and plot of $1/[PhOTos]_t$ versus time was given in Fig. 1. The second order rate constants, k were calculated by linear regression analysis to be (i) $15.5 \cdot 10^{-3}$ M^{-1} min^{-1} (r=0.9963), (ii) $15.1 \cdot 10^{-3}$ M^{-1} min^{-1} (r=0.9979) and (iii) $13.8 \cdot 10^{-3}$ M^{-1} min^{-1} (r=0.9947), respectively. The rate constants (i) and (ii) are almost equal; in the error limit 4-9±% of GLC analysis. The rate constant (iii) is somewhat lower than (i) and (ii), possibly due to the difficulty in the GLC analysis of phenol (**4)**. However, we included the rate constant (iii) as a second support to the rate contant (i) and we did not take this discrepancy into consideration in the evaluation of rate data.

As seen, the use of measured and calculated values of $[PhOTos]_t$ values did not make appreciable change in the evaluation of second order kinetics. This observation supports the conclusion that phenyl tosylate reacts with phenylmagnesium bromide to give sulfone as the sole product and also phenylmagnesium bromide does not react further with sulfone.

(b) We also evaluated the rate data collected under pseudo-first order conditions *i.e.* in the presence of excess and varied phenyl magnesium bromide, expecting a linear dependence of pseudo-first order rate constants upon the concentration of reagent. For this purpose, the initial concentration of phenyl tosylate **(2)** vas kept constant at 0.026 M and concentration of phenylmagnesium bromide **(1a)** was varied between 10-22 times that of **(2)**. The rate data were evaluated as pseudo-first order and also pseudo-zero order in **(2)**. We used directly calculated $[PhOTos]_t$ values to minimize the errors resulting from the indirect calculations of $[PhOTos]_t$ value. Zero order plots were curved, but first order plots, *i.e.* plots of log $[PhOTos]_t$ values versus time proved linear to at least 60% completion of the reaction (Fig. 2). Pseudo-first order rate constants, k_1 were calculated by linear regression analysis ($r \geq 0.99$) and are given in Table 1. The linearity of k_1 values with excess concentration of phenyl magnesium bromide **(1a)** is illustrated in Fig. 3. Plots of log k_1 versus log [PhMgBr] yielded a slope of 1.01 (r=0.9838) confirming the first order reaction in Grignard reagent.

The second order rate constants, k were calculated as $k=k_1/[PhMgBr]$ and taking the average led to $k=13.0 \times 10^{-3} \pm 0.9$ M^{-1} min^{-1} with the uncertainty of ± 7%.

Table 1. Effect of phenylmagnesium bromide (**1a**) concentration on the reaction rate of phenyl magnesium bromide (**1a**) with phenyl tosylate (**2**) in THF: toluene (7:10) at 90°C.[a]

$[C_6H_5MgBr]$, M	10^3k1, min^{-1}	10^3k, M^{-1} min^{-1} [b]
0.261	3.25	12.4
0.336	4.80	14.3
0.410	4.77	11.6
0.485	6.12	12.6
0.560	7.79	13.9

[a] *[PhOTos]o= 0.026M*
[b] *k=k1/ [C6H5MgBr]*

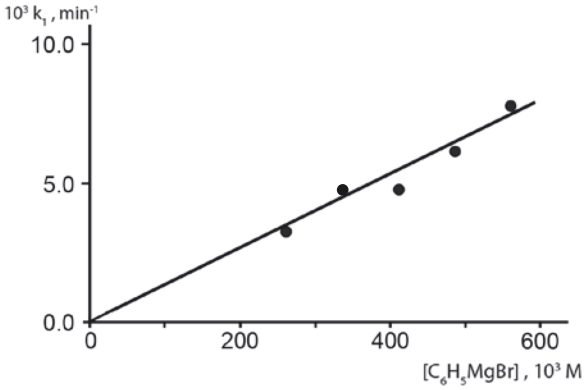


Figure 3. Effect of phenyl magnesium bromide (**1a**) concentration on the pseudo-first order rate constants for the reaction of phenyl magnesium bromide (**1a**) with phenyl tosylate (**2**) in THF: toluene (7:10) at 90°C. Data are from Table 1.

As seen, calculation of the second order rate constants by applying second order conditions or pseudo-first order conditions resulted in the same values within the error limit. This result provides another evidence for the second order kinetics of C-S coupling of aryl Grignard reagents with sulfonates.

The rate law for the reaction of phenylmagnesium bromide (**1a)** with phenyl tosylate **2** can be expressed as

$$-\frac{d[PhOTos]}{dt} = k\,[ArMgBr][PhOTos] \qquad (1)$$

For purposes of discussion, kinetic orders can be assumed to be 1. Arylmagnesium bromide species are demonstrated as ArMgBr rather than $(ArMgBr)_2$ –bridged dimers since all alkyl and arylmagnesium halides are known to be monomeric in THF over a wide concentration range (0.1-3.5 M) [39,40]. Arylmagnesium halides are also incapable of homolysis, aryl radicals being extremely unstable [41]. So the transfer of one electron to sulfonate is very unlikely. In conclusion, the first order kinetics in aryl Grignard reagent and in phenyl tosylate in their reaction to yield sulfones seems consistent with the rate determining nucleophilic attack of Grignard species derived carbanion at sulfonate sulfur.

In this research, we used a Hammett correlation for the substituent effects of the nucleophile, *i.e.* aryl Grignard reagents and also calculated activation parameters to gain insight into the mechanism [42].

For Hammett study, we measured the rate constants of alkyl –, alkoxyl– and bromosubstituted phenylmagnesium bromides with phenyl tosylate in THF:toluene at 90°C and these substituents allowed us to try ρ–σ correlation for the reaction. For this purpose, we evaluated the rate data under pseudo–first order conditions using directly calculated $[PhOTos]_t$ values versus time. For the reaction of each aryl Grignard reagent, we observed linear dependence of pseudo–first order rate constants upon the concentration of excess Grignard reagent. The second order rate constants are given in Table 2 and the plot of rate constants against the standard Hammett σ values is shown in Fig. 4.

Table 2. Rate constants for the sulfonation of substituted phenylmagnesium bromides (**1a–g**) with phenyl tosylate (**2**) in THF:toluene (7:10) at 90°C.

Compound	Substituent, X	σ [a]	10^3 k M^{-1} min^{-1} [b]
1d	4–$(CH_3)_3C$	–0.15	25.0
1b	4–CH_3	–0.14	21.3
1e	4–CH_3O	–0.12	43.2
1c	3–CH_3	–0.06	17.0
1a	H	0.00	13.0
1f	3–CH_3O	0.10	14.2
1g	4–Br	0.26	7.4

[a] *Substituent constants are taken from Ref.42.*
[b] *Second orden rate constants were calculated under pseudo–first orden conditions.*

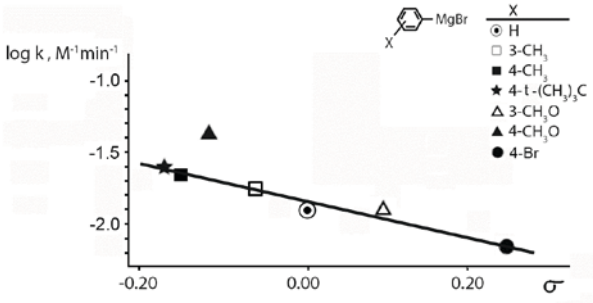
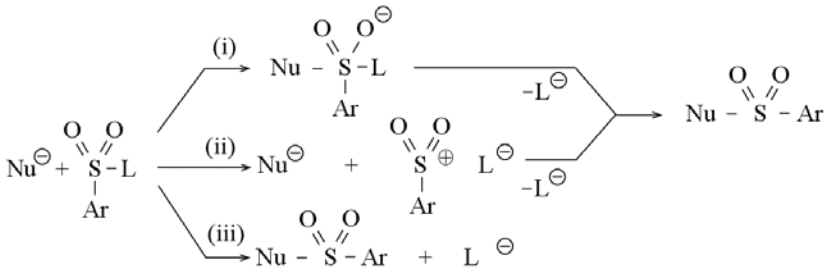


Figure 4. Hammett plot for the rate constants of substituted phenylmagnesium bromides (**1a–1d, 1f, 1g**) with phenyl tosylate (**2**) in THF:toluene (7:10) at 90°C.

As seen, a reasonably good ρ–σ correlation with a value of ρ = –1.19 (r = 0.959) was obtained for C-S coupling of Grignard reagents with aryl arenesulfonates. For the correlation, we did not use the point for the 4—CH_3O substituent lying significantly off the linear plot. In fact, deviations have been already reported with 4–CH_3O and also with 4–Br and 3–Br containing phenylmagnesium reagents in the Hammett plots for their reactions [43-45].

We also calculated the activation enthalpy, $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ for the sulfonation of phenylmagnesium bromide **1a** with phenyl tosylate **(2)**. The second order rate constants, k of the reaction of **(1a)** with **(2)** were calculated at different temperatures and k were obtained to be 13.0 $M^{-1}min^{-1}$ (From the data in Table 2), 11.8 $M^{-1}min^{-1}$, 8.9 $M^{-1}min^{-1}$ and 7.3 $M^{-1}min^{-1}$ at 90.0°C, 85.0°C, 80.0°C and 75.0°C, respectively. Eyring plot of ln(k/T) versus 1/T was found linear (r=0.983) (Fig. 5) and activation parameters $\Delta H^{\neq}$= 35.9∓1.7 kJ mol^{-1} and $\Delta S^{\neq}$= -182.2∓4.2 J mol^{-1} K^{-1} were determined from the slope and intercept,



Scheme 3. Sulfonyl transfer reactions of aryl arenesulfonates (L:OAr) and aryl sulfonyl halides (L:halogen) with nucleophiles.(i) S_Na (addition-elimination) mechanism, (ii) S_N1(S) mechanism, (iii) S_N2(S) mechanism.

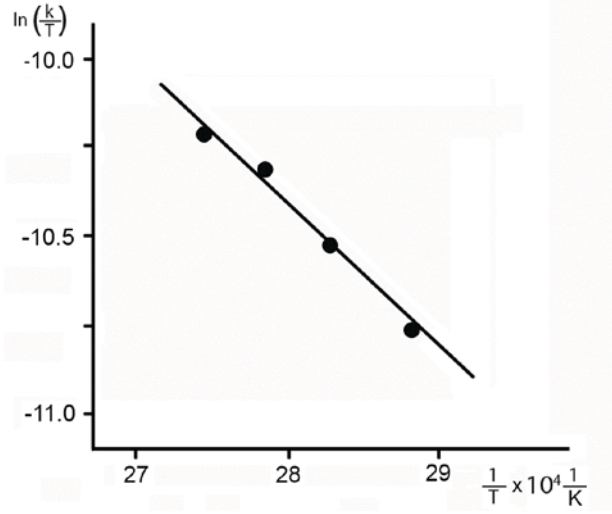


Figure 5. Eyring plot for the reaction of phenylmagnesium bromide (**1a**) with phenyl tosylate (**2**) in THF:toluene (7:10).

respectively of line [46,47]. The uncertainties in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined from the mean deviation in the slope and intercept of the line, respectively.

4. Discussion

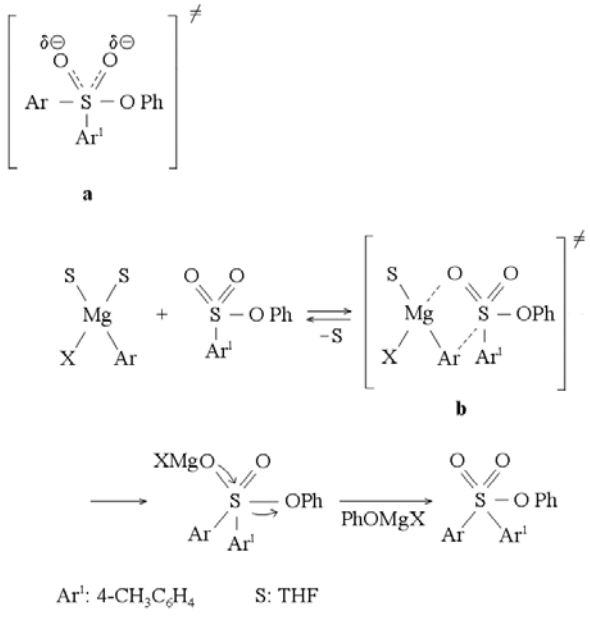
Sulfonyl transfer reactions of arenesulfonic acid derivatives bearing phenoxides or halides as leaving group are expected to take place by three different mechanisms (Scheme 3): [31] (i) addition-elimination S_Na mechanism involves a pentavalent complex [31-34]; (ii) stepwise S_N1(S) mechanism is expected to proceed via an incipient sulfonylium cation [35]; (iii) concerted S_N2(S) mechanism proceeds via a transition state in which bond formation and bond breaking occurs synchronously [31-34]. Sulfonyl group transfer is associative in mechanisms (i) and (iii) and dissociative in mechanism (ii).

A number of investigations have been already reported using linear free energy relationships to distinguish between concerted S_N2(S) and stepwise S_Na mechanisms for the nucleophilic substitution of aryl arenesulfonates at sulfur atom [32-35]. The generally accepted mechanism is a concerted synchronous S_N2(S) mechanism in which nucleophilic attack to sulfur and leaving group departure occurs in a single step [32-34].

We tried Hammett treatment of substituent effects [40] in the reaction of aryl Grignard reagents with aryl arenesulfonates. In fact, to elucidate the transition state structure in the rate determining step, substituent constants should be carefully chosen not only for the substituents on the nucleophile [33,34], but also for the substituents on the arenesulfonyl group [33-35] and on the leaving group [32-34].

For the substituents on the nucleophile, the use of σ constants gives a good correlation if the reaction is concerted S_N2 or if elimination of the leaving group is rate determining step in the S_Na nechanism. In these cases, direct interaction of substituents with negative charge on the nucleophile would not affect bond formation in the rate determining step. A good correlation with σ^- constants is obtained if addition is the rate determining step in the S_Na mechanism, or if bond formation to the nucleophile is well advanced and bond breakage to the leaving group is minimal in the S_N2 mechanism. In both cases, delocalization of the nucleophilic charge with substituents would result in a change in the nucleophilicity and also in the bond formation.

In summary, Hammett correlations with σ^- constants as well as σ constans should be tried to get information about the mechanism. However, ρ–σ^- correlations require finding rate constants of aryl Grignard reagents with –M substituents, such as carbonyl, cyano and nitro, at para position to the nucleophilic carbon and these Grignard reagents can not be used at temperatures higher than 0°C. So, we could try only ρ–σ correlation and found that the reaction has a significant negative ρ value, suggesting that the reaction process involves thiophilic attack of a substituted carbanion on the sulfonate. However this result does not seem to help us to make a clear distinction between a concerted S_N2 mechanism and S_Na mechanism ın which addition or elimination is the rate deterrmining step. Nevertheless, it seemed to us conceivable to suggest that C-S coupling proceeds through a S_N2 mechanism involving a



Scheme 4. Proposed mechanism for C-S coupling of aryl Grignard reagents with aryl arenesulfonates.

transition state in which carbanion and phenoxy groups are bound to sulfur (Scheme 4a). Similar substituent effects of nucleophiles have been reported in the Hammett treatment of rate constants for the nucleophilic substitution at arenesulfonates [33].

In our synthetic investigation, we used THF:toluene (1:10) as a solvent since we observed that the yield decreases as THF: toluene ratio increases [30]. Higher yields and/or higher reaction rates were observed in a number of reactions of Grignard reagents when toluene or toluene–diethyl ether (or THF) was used instead of ethereal solvent [48,49]. So, in discussing the concerted S_N2 mechanism of Grignard C-S coupling with sulfonate esters, the solvation of Grignard reagents in THF: toluene and also the electrophilicity of sulfur atom in arenesulfonates with a good leaving group, *i.e.* phenolate also seemed critical.

In THF: toluene, the solvation of Grignard reagent by donor THF does not change, however the Grignard reagent is partially solvated and nucleophilic solvation of arenesulfonate oxygen atoms may appear. For the mechanism of sulfonate addition of Grignard reagent, we first decided to start thinking in an analogous fashion to carbonyl addition of Grignard reagents. The reaction can proceed through a four–center transition state [50] (Scheme 4b). The coordination of the ester with Mg occurs by replacement of donor THF coordinated to Grignard reagent. Nucleophilic solvation of Mg leads to polarization of the C–Mg bond and an increase both in the nucleophilicity of the carbanion and in the electrophilicity of S in sulfonyl group. Then, replacement of donor THF by a noncomplexing solvent, *i.e.* toluene will result in a more favorable complex formation of the sulfonate with Grignard reagent leading to observed reactivity of aryl Grignard reagents for C–S coupling in THF:toluene.

In the reaction of phenylmagnesium bromide with phenyl tosylate we already used HMPA as a cosolvent in THF:toluene and we observed that the sulfonation yield decreases as HMPA:THF ratio increases [51]. We can think that, HMPA being a coordinating solvent results in a less favorable complex formation of the sulfonate with Grignard reagent as, expected.

The reactivity of arene sulfonates as S electrophiles may be also ascribed to the Lewis acidity of Grignard reagents. However, we already carried out the reaction of phenylmagnesium bromide with phenyl tosylate in the presence of 10 mol% $MgCl_2$, *i.e.* an external Lewis acid, but the sulfonation yield decreased [51]. This implies that nucleophilic solvation of MgBr $^{\delta\oplus}$ in RMgBr or in other words internal electrophilic catalysis of RMgBr works better than catalysis of $MgCl_2$. Metal ion stabilization of the transition state due to the chelation of metal by oxygen atoms in the sulfonyl moiety was also reported in the reactions of aryl benzenesulfonates with alkali–metal ethoxides [32].

It is known that [46,47] in S_N2 reactions, activation entropies should be negative, but depending upon the charge type in the formation of transition state and also upon the solvation, the range of $\Delta S^{\neq}$ values change. For charge separation, numerical values of activation entropies were reported to be –90–(–120) J $K^{-1}mol^{-1}$ whereas lower mumerical values *i.e.*–20–(–40) J K^{-1} mol^{-1} were reported for charge delocalization. Comprehensive studies on the hydrolysis of arenesulfonates also provided convincing evidence that sulfonyl transfer in an associative process leads to large negative values $\Delta H^{\neq}$ with low values of $\Delta H^{\neq}$ [35].

The relatively low value of $\Delta H^{\neq}$ and the large negative value of $\Delta S^{\neq}$ found for the reaction of phenyl magnesium bromide **1a** with phenyl tosylate **2** suggest that the reaction might follow an associative process in the formation of transition state as expected.

The present study on the sulfonyl transfer reaction of aryl Grignard reagents with phenyl tosylate has allowed us to draw the following conclusions:

(1) The first order kinetics in aryl Grignard reagent and in phenyl tosylate seems consistent with the nucleophilic attack of aryl carbanion to sulfonyl group.

(2) In THF:toluene, Grignard reagent is partially solvated and coordination of ester with Mg occurs by replacement of donor THF coordinated to Grignard reagent. Nucleophilic solvation of Mg leads to polarization of C–Mg bond and results in an increase in the nucleophilicity of the carbanion to electrophilic sulfur

in the sulfonyl group.

(3) Hammett ρ–σ correlation for the substituted aryl Grignard reagents yields a good correlation.

(4) The large negative value of activation entropy is consistent with an associative process in which the rate of reaction is determined by C–S formation in the transition state.

(5) These results imply that sulfonyl transfer possibly proceeds via a single step concerted S_N2 mechanism, but do not allow us to decide between a synchronous mechanism or an asynchronous mechanism in which carbanion attack possibly takes place ahead of phenoxy group departure in the transition state.

In our continuing work, we will study on the substituent effects of arenesulfonyl and aryloxy groups, and also investigate the solvent effects to provide evidence regarding the synchrony of the proposed S_N2 mechanism for the sulfonyl transfer reaction of aryl Grignard reagents.

Acknowledgement

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