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## 161. Mechanisms of Diazo Coupling Reactions. Part XXX. *N*-Diazo Coupling of *p*-Chloroaniline in Acetonitrile: Rate-Limiting Proton Transfer<sup>1)</sup>

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### Summary

The *N*-diazo coupling of *p*-chloroaniline with *p*-chlorobenzenediazonium tetrafluoroborate in acetonitrile at 30° shows non-linear base catalysis by water. The results are interpreted in terms of the  $S_E2$  mechanism with rate-limiting proton loss at low base concentration; it is postulated, moreover that the reaction proceeds *via* transition states in which varying degrees of H-bonding from the amine and the intermediate  $\sigma$ -complex to different water species influence the initial step and the base catalysis.

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**1. Introduction.** - In an earlier communication [1] we reported that *N,N*-dimethylaniline and *m*-toluidine react with *p*-methoxybenzenediazonium tetrafluoroborate to form the corresponding aminoazo compounds in acetonitrile (*C*-coupling). In the presence of the strong base tetramethylammonium chloride, however, there is a large increase in reaction rate and diazoamino compounds (with loss of a methyl group in the case of *N,N*-dimethylaniline) are formed in *ca.* 100% yield (*N*-coupling). The mechanism of aminoazo formation in the absence of base is considered in a later publication [2]. It will be clear that the mechanistic consideration of this reaction is aided by a knowledge of the mechanism of diazoamino formation, and it is the purpose of this communication to establish this mechanism.

It has long been known from extensive investigations (for a summary of the earlier work see [3]) that under aqueous conditions the formation of aminoazo compounds can be base-catalyzed and this is due to rate-limiting proton loss from the  $\sigma$ -complex in the  $S_E2$  mechanism. Further, there is evidence to suggest that *C*-diazo coupling takes place *via* a donor-acceptor complex formed between the diazonium ion and the substrate [4]. In aprotic solvents, both rate-limiting proton loss and molecular complex formation can occur [2].

The mechanism of the formation of diazoamino compounds has been less extensively investigated, however it would appear to be similar to that of *C*-

<sup>1)</sup> Part XXIX, see [1].

coupling. Thus in ethanol/water 80:20 (v/v), it has been found that  $\rho$ -values for the C- and N-coupling of *N*-methylaniline are similar [5], and in a Russian report on the N-coupling of *p*-toluidine and diethylaniline with several substituted benzenediazonium salts in polar aprotic media it is claimed that the reaction shows general base catalysis and involves an 'early' transition state [6]. It has been known for some time that under suitable conditions, N-coupling, in contrast to C-coupling<sup>2)</sup>, can be reversible (for a summary of the earlier work, see [8]). Treatment of diazoamino compounds with acid, usually carried out in the corresponding amine solvent, can produce aminoazo compounds which, according to the so-called *Friswell-Green* mechanism, are formed *via* free diazonium ion produced by fast fission of the protonated diazoamino compound. The rate-determining step was thought to be attack of the diazonium ion at C-atom (perhaps with rate-limiting proton loss). However, doubts have been raised concerning this mechanism [8], and in the rearrangement of *N*-methyldiazoamino compounds in ethanol/water 95:5 [9], the results suggest rate-limiting dissociation of the protonated diazoamino compound.

According to the principle of microscopic reversibility, in the reverse N-coupling reaction of the *N*-methylaniline, attack of the diazonium ion at amine N-atom should be rate-determining, and the reaction should not be subject to base catalysis.

It thus appears that N-coupling, like C-coupling, can show base catalysis or not, depending on the conditions, *i.e.* solvent, nature of substrate and diazonium ion, and it was to determine whether or not the base catalysis of N-coupling observed previously [1] is due to rate-limiting proton loss from the  $\sigma$ -complex in the  $S_E2$  mechanism that this investigation was undertaken.

**2. Results.** - Preliminary investigation confirmed that the N-coupling reactions of aniline and a number of substituted anilines (*p*-chloro, *N,N*-dimethyl, *p*-methoxy-, *m*-methyl, *p*-methyl-,) with a number of diazonium tetrafluoroborates (*p*-chloro-, *p*-methoxy-, *p*-methyl-,) were catalyzed by *t*-butylammonium chloride in dry acetonitrile. Further, other species, *e.g.* pyridine and dimethylsulfoxide (DMSO), were capable of accelerating the reactions. A full investigation was carried out of the reaction between *p*-chloroaniline and *p*-chlorobenzenediazonium tetrafluoroborate. Rates easily measurable using the conventional technique were obtainable with this system, and complications due to possible aminoazo formation (which occurs with *m*-toluidine and *N*-methylaniline) and tautomerism are avoided. The reaction was investigated in dry acetonitrile to avoid base catalysis due to traces of water, and all handling operations performed in a nitrogen dry box to preclude contamination by atmospheric water. The solvent was deoxygenated before drying in order to reproduce the conditions used in our earlier work [1]. Rates were measured by following the increase in product with time spectrophotometrically (at 355 nm).

In the absence of any additive and under pseudo first-order conditions (> 10 times excess amine concentration) the reaction was first-order with respect to diazonium ion and showed an order with respect to amine of ca. 1.8 in the range 0.05-0.2 M. However, first-order plots to determine the rate

<sup>2)</sup> It has been shown that a C-coupling can be reversible, but under (relatively) rigorous conditions [7].

constant were not particularly good and the runs not easily reproducible ( $\pm 10\%$ ). The reason for this is not clear.

The effect of a number of additives on the reaction was investigated (*Table 1*, column 1).

The reaction is catalyzed strongly by (relatively) strong bases in the order  $\text{H}_2\text{O} < \text{dimethylformamide (DMF)} < \text{pyridine} < \text{DMSO} < \text{hexamethylphosphoramide (HMPT)}$ , but even acetone is capable of increasing the rate. With these catalyzed reactions, excellent first-order plots were found, and reproducibility was good. For purposes of comparison, the C-coupling reactions of 1- and 2-naphthylamine with *p*-methyl- resp. *p*-chlorobenzenediazonium tetrafluoroborate were investigated; the *p*-chloro derivative gave, unfortunately, too fast a rate even at very low amine concentration for accurate measurement<sup>3</sup>). Tests with additive *t*-butylammonium chloride had established that these C-coupling reactions were catalyzed by base, and the product spectrum is the same if the reaction was carried out in presence of the catalyst or not. *Table 1*, columns 2 and 3, shows that HMPT is also the strongest catalyst in these reactions, but in contrast to *N*-coupling, pyridine is more effective than DMSO. With the last five additives in the *Table* the order with respect to additive is *ca.* 1.

Attempts were made with all additives to observe a limiting rate independent of additive concentration. This was only unambiguously possible with water where quantitative yields were obtained (*Fig. 1*). All other additives decomposed the diazonium salt at the high concentrations (3–20%, *v/v*) used. The maximum rates observed with several additives are shown in *Table 2*. With DMF and DMSO, a limiting rate was observed at *ca.* 20% (*v/v*) additive, but this was accompanied by low (*ca.* 70%) yields, and above this concentration the rate actually decreased slightly. The very

*Table 1. The relative ability of additives to catalyze the N-coupling of p-chloroaniline with p-chlorobenzenediazonium tetrafluoroborate, and the C-couplings of 1- and 2-naphthylamine with p-methylbenzenediazonium tetrafluoroborate in acetonitrile at 30°<sup>a</sup>)*

Amine/additive	<i>p</i> -Chloroaniline	1-Naphthylamine <sup>b</sup> )	2-Naphthylamine <sup>c</sup> )
(CH <sub>3</sub> ) <sub>2</sub> C=O <sup>d</sup> )	0.04	–	–
THF	0.20	–	–
EtOH	0.36	–	–
MeOH	0.39	–	–
H <sub>2</sub> O <sup>e</sup> )	1	1	1
DMF <sup>e</sup> )	5	20	24
Pyridine <sup>e</sup> )	8	307	321
DMSO <sup>e</sup> )	15	93	151
HMPT <sup>e</sup> )	220	1380	1490

<sup>a</sup>) [Amine]  $\geq 10 \times$  [diazonium salt]. Measured under conditions of linear base catalysis. <sup>b</sup>) At 425 nm. <sup>c</sup>) At 435 nm. <sup>d</sup>) Addition of 0.85M acetone increases pseudo first-order rate constant from  $2.57 \times 10^{-3} \text{ s}^{-1}$  to  $3.65 \times 10^{-3} \text{ s}^{-1}$ . <sup>e</sup>) In all three coupling reactions the concentration of additive was the same or similar.

<sup>3</sup>) The change in diazonium salt is not, however, expected to change the relative ability of the additives to catalyze the reaction.

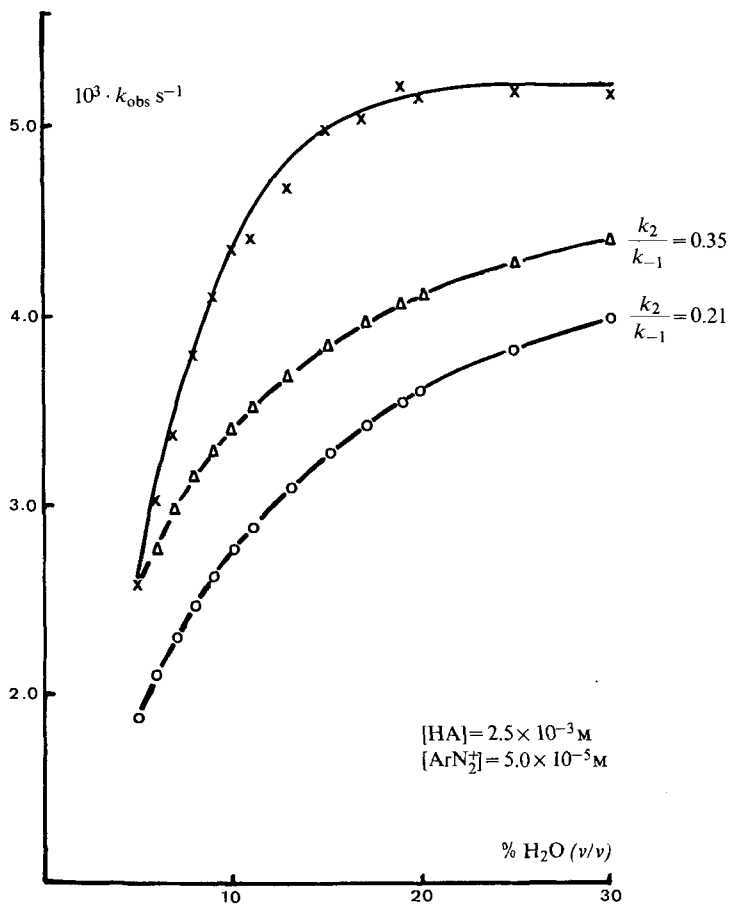


Fig. 1. Catalysis by water of N-coupling of p-chloroaniline (HA) with p-chlorobenzenediazonium tetrafluoroborate ( $\text{ArN}_2^+$ ) in acetonitrile at  $30^\circ$ . Experimental points (x); theoretical points ( $\Delta$  and o, see Fig. 2).

Table 2. Maximum rates observable with different additives in the N-coupling of p-chloroaniline with p-chlorobenzenediazonium tetrafluoroborate in acetonitrile at  $30^\circ$

Additive (v/v)	$k_{\text{obs}}/[\text{Amine}]^3$
20% DMF <sup>b)</sup>	1.9
25% H <sub>2</sub> O	2.1
20% DMSO <sup>b)</sup>	8.6
3.3% HMPT <sup>c)</sup>	31.4
( <i>t</i> -But) <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup> ( $2.0 \times 10^{-2}$ M)	180.5

a)  $1 \text{ mol}^{-1} \text{ s}^{-1}$ . b) Both the rate and product yield decrease above this concentration. c) Yield ca. 70%. At double the concentration shown the yield is too low to allow accurate rate measurements.

strong catalysis by chloride ion and HMPT is shown by the fact that rates of *ca.* 95 and 17 times, respectively, greater than the limiting rate in water can be observed.

The experimental line (x) in *Figure 1* shows that a limiting rate ( $k_{\text{obs}} = 5.14 \times 10^{-3} \text{ s}^{-1}$ ,  $[\text{HA}] = 2.5 \times 10^{-3} \text{ M}$ ) is reached at *ca.* 11 M  $\text{H}_2\text{O}$ . At the limiting rate, an increase in amine concentration doubles the rate, thereby excluding lack of solubility of the amine as the factor responsible. From a plot of  $1/k_{\text{obs}}$  against  $1/[\text{H}_2\text{O}]$  (*Fig. 2*) it is possible to obtain values of  $Kk_1$  and  $k_2/k_{-1}$  (see following section) and to use these to calculate the theoretical change in  $k_{\text{obs}}$  with base concentration. Two theoretical lines (*l* and *o*) are shown in *Figure 1*. Clearly, an explanation is required for the discrepancy between these and the experimental curve.

There appears to be no change in N-H(D) isotope effect with  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ) content. Thus a small isotope effect is observed at 5% (v/v)  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ) of

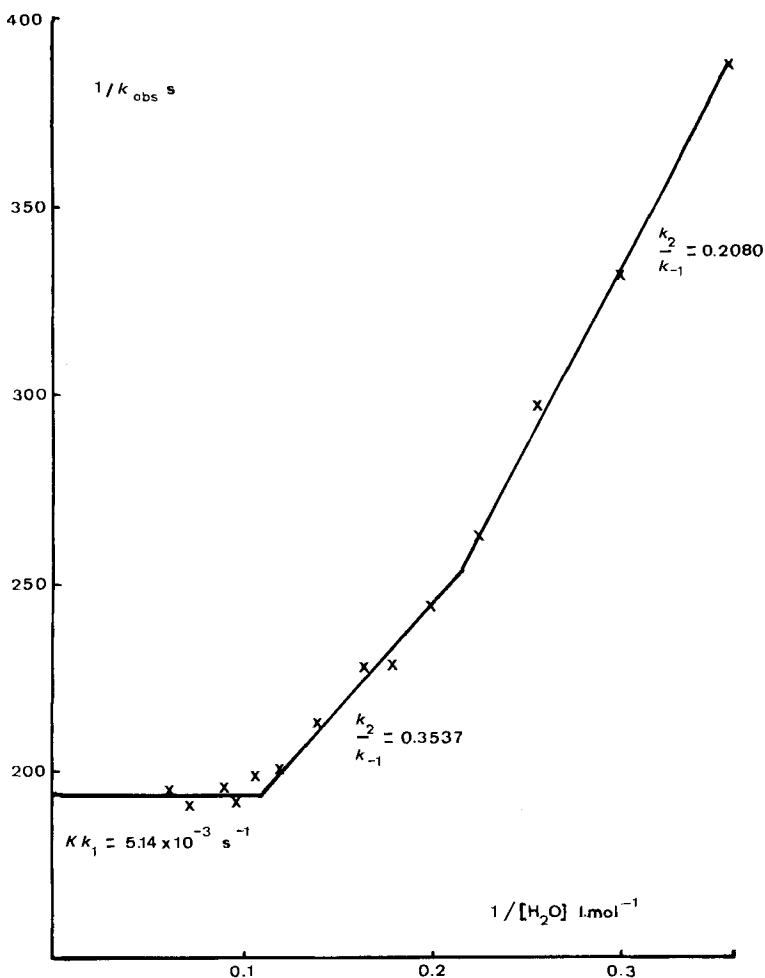


Fig. 2. Plot of  $1/k_{\text{obs}}$  against  $1/[\text{H}_2\text{O}]$  for N-coupling of p-chloroaniline (HA) with p-chlorobenzene-diazonium tetrafluoroborate in acetonitrile at 30°.

Table 3. The effect of *t*-butylammonium chloride on the coupling of *p*-chloroaniline with *p*-chlorobenzene-diazonium tetrafluoroborate in acetonitrile at 30° in the presence of H<sub>2</sub>O or DMF

[( <i>t</i> -But) <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup> ]	( <i>v/v</i> )% H <sub>2</sub> O	<i>k</i> <sub>obs</sub> /[Amine] <sup>a</sup>
-	10	1.40
1.00 × 10 <sup>-2</sup>	10	1.80
4.80 × 10 <sup>-2</sup>	10	2.12
1.24 × 10 <sup>-1</sup>	10	3.74
	( <i>v/v</i> )% DMF	
-	10	1.44
1.00 × 10 <sup>-2</sup>	10	57.42
5.45 × 10 <sup>-2</sup>	10	179.20

<sup>a</sup>) 1 mol<sup>-1</sup> s<sup>-1</sup>.

Table 4. Isotope effects in the acid catalyzed decomposition of 4,4'-dichlorodiazaminobenzene<sup>a</sup>) in acetonitrile at 30°

( <i>v/v</i> )% H <sub>2</sub> O or D <sub>2</sub> O	[Acid] <sup>b</sup> ) (M)	<i>k</i> <sub>D<sub>2</sub>O</sub> / <i>k</i> <sub>H<sub>2</sub>O</sub> <sup>c</sup> )
1	5.06 × 10 <sup>-4</sup>	0.81
5	5.06 × 10 <sup>-4</sup>	1.37
30	5.06 × 10 <sup>-4</sup>	1.91

<sup>a</sup>) 5 × 10<sup>-5</sup>M. <sup>b</sup>) *p*-Cl-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> or *p*-Cl-C<sub>6</sub>H<sub>4</sub>-ND<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>. <sup>c</sup>) Ratio of pseudo first-order rate constants.

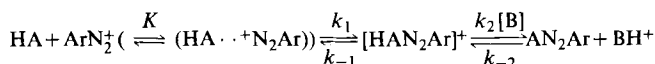
*k*<sub>H</sub>/*k*<sub>D</sub> = 1.10 ± 5%, but this still persists after the limiting rate has been reached: *k*<sub>H</sub>/*k*<sub>D</sub> = 1.15 ± 5% at 30% (*v/v*) H<sub>2</sub>O (D<sub>2</sub>O).

Close to the limiting rate with additive water, the reaction is catalyzed by chloride ion. Table 3 shows that addition of 0.124M *t*-butylammonium chloride increase the rate by a factor of 2.7. With DMF, at a concentration again close to that where a limiting rate may be reached, this catalysis is much more marked (ca. 125x), presumably due to the increased activity of the chloride ion.

Finally, the reverse reaction of the *N*-coupling, the acid catalyzed decomposition of 4,4'-dichlorodiazaminobenzene was measured in the presence of 1, 5 and 30% (*v/v*) H<sub>2</sub>O or D<sub>2</sub>O. The reaction is first-order in diazoamino compound and much slower than the *N*-coupling under identical conditions. As Table 4 shows, at low H<sub>2</sub>O or D<sub>2</sub>O content the reaction in H<sub>2</sub>O is faster, whereas it is slower in 30% (*v/v*) additive. At the highest water content, the reverse reaction is not negligible and the appropriate equation must be used to calculate the rate constant [10]. Good first-order plots were obtained for all runs.

**3. Discussion.** - In view of the apparent similarity between *C*- and *N*-coupling mentioned in the Introduction, the latter is best considered initially in terms of the *S*<sub>E</sub>2 mechanism known to apply to the formation of aminoazo compounds with step 2 showing base catalysis. This is shown in Scheme 1, but includes the reverse reaction of step 2. Under the conditions of nearly all of our experiments, particularly those carried out in the presence of water, rearrangement of the product is so much slower than *N*-coupling that it can be safely ignored, i.e. *k*<sub>-2</sub> is very small. Scheme 1

## Scheme 1



HA Amine;  $\text{ArN}_2^+$  Diazonium ion; B Any base, *i.e.* amine, solvent, anion of diazonium salt, additive.

also shows the formation of a molecular complex between the amine and the diazonium ion. We have no evidence under the present conditions for the existence of such a complex, however, this has been demonstrated for other diazo coupling reactions under aqueous conditions [4] and in a later publication we shall present indirect evidence to show that such complexes are probably formed in acetonitrile [2]. The observed pseudo first-order rate constant for the reaction, neglecting  $k_{-2}$ , is given by equation 1.

$$k_{\text{obs}} = \frac{K[\text{HA}]}{1 + K[\text{HA}]} \frac{k_1 k_2 [\text{B}]}{k_{-1} + k_2 [\text{B}]} \quad (1)$$

We shall first consider the situation prevailing in the catalysis by water of the reaction (*Fig. 1* and 2). At high water content, the order with respect to [HA] is 1.0 suggesting  $K[\text{HA}] \ll 1$ . When the two limiting situations are considered, the following equations for  $k_{\text{obs}}$  are obtained.

$k_2[\text{B}]/k_{-1}$	$k_{\text{obs}}$
$\ll 1$	$K[\text{HA}] \cdot \frac{k_1 k_2 [\text{B}]}{k_{-1}}$
$\gg 1$	$K[\text{HA}] k_1$

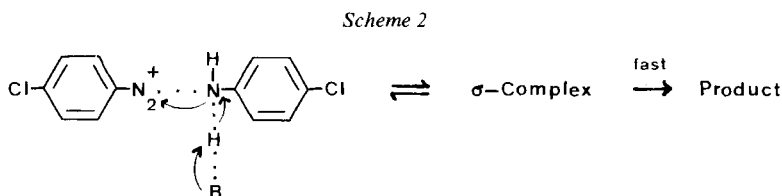
At low [B], the reaction is dependent on [B] to the first power, whereas a limiting rate independent of [B], is predicted at high [B]. This is exactly the situation we observe with, however, certain limitations. Thus, *Figure 1* shows that when  $Kk_1$ - and  $k_2/k_{-1}$ -values of *Figure 2* are used to calculate  $k_{\text{obs}}$  at different water concentrations, the fall-off in rate is less rapid than observed experimentally. As *Figure 2* shows, it is extremely difficult to obtain an accurate value for  $k_2/k_{-1}$  due to the difficulty in obtaining an accurate value for the slope. Two extreme values have been used, but whatever value is taken for this, the fall-off in experimental rate is still too fast, although the difference is not great. In the experiments reported, at the lowest concentration of water the order with respect to water was 1, hence there is no contribution of the solvent, amine or anion of the diazonium salt to the base catalysis under these conditions.

A further, less disturbing result, is the observation that the N-H(D) isotope effect does not change with  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ) content. In the formation of aminoazo compounds by the  $S_{\text{E}}2$  mechanism with rate-limiting proton loss from C-atom,  $k_{\text{H}}/k_{\text{D}}$  is generally substantially greater than 1. However, for rate-limiting proton loss from N-atom the situation is unclear; thus under conditions which are expected

to lead to a maximum isotope effect,  $k_H/k_D = 1$  [11]. We are therefore of the opinion that our results do not preclude the operation of the  $S_E2$  mechanism, especially in view of the suggestion that  $N$ -coupling involves an 'early' transition state [6], and hence very little stretching of the  $N-H$  bond is expected.

However, because of these difficulties we considered at first that the observed acceleration by base is due to catalysis of a step other than proton loss from the  $\sigma$ -complex. The observation of a limiting rate with added water and possibly DMF and DMSO effectively rules out a concerted mechanism in which in the transition state the  $N, H$ -bond of the amine is stretched at the same time as the diazonium ion attacks amine  $N$ -atom. We cannot, however, definitely eliminate such a mechanism in cases where a limiting rate has not been observed, namely in reactions with added chloride ion and HMPT.

A second pathway of catalysis is possible in which in the  $S_E2$  mechanism the rate is accelerated by base catalysis of step 1, the formation of the  $\sigma$ -complex. Such a mechanism would involve stretching of the  $N, H$ -bond in a molecular complex  $HA \cdots ^+N_2Ar$  followed by attack of the diazonium ion at amine  $N$ -atom to form the  $\sigma$ -complex and fast proton loss (*Scheme 2*)<sup>4</sup>.



While such a mechanism can explain the relative catalytic abilities of different additives by their ability to stretch the  $N, H$ -bond it is difficult to envisage the attainment of a limiting rate (we shall, however, return to the implications of possible non rate-limiting catalysis of step 1 in the  $S_E2$  mechanism later). Further, in the reverse reaction, the acid catalyzed decomposition of 4,4'-dichlorodiazaminobenzene (*Table 4*), there should be no change in  $k_{D_2O}/k_{H_2O}$  with solvent composition. The results are consistent with a fast pre-equilibrium proton transfer at high  $H_2O$  ( $D_2O$ ) content and the value  $k_{D_2O}/k_{H_2O} = 0.81$  is suggestive of a rate-determining proton transfer at low  $H_2O$  ( $D_2O$ ) content. According to the principle of microscopic reversibility, this is consistent with the operation of the  $S_E2$  mechanism in the  $N$ -coupling reaction. A similar situation has been found in the *Fischer-Hepp* rearrangement of  $N$ -methyl- $N$ -nitrosoaniline in ethanol [12], where rate-determining proton transfer has been found, but as water is added to the solvent, decomposition of the intermediate becomes rate-limiting.

Thus our results do not support the operation of any 'unusual' mechanism, but are consistent with the  $S_E2$  mechanism showing rate-limiting proton loss with the exception of the non-linear base catalyzed region between 5 and 20% ( $v/v$ ) water

<sup>4</sup>) Attack of the diazonium ion can be assumed to occur on the solvated amine.



in the plot  $k_{\text{obs}}/[\text{H}_2\text{O}]$  (Fig. 1). If the observations with DMF and DMSO are not caused by an artifact resulting from low (ca. 70%) yield of product, then a similar phenomenon occurs with these additives.

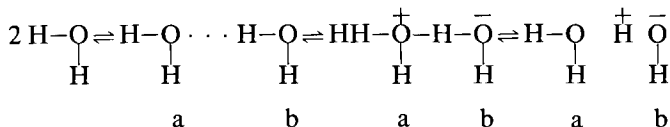
We have considered several possibilities to explain this anomaly of the  $S_E2$  mechanism.

The diazonium ion does not appear to be strongly solvated in a variety of solvents [13] [14] and ion pairing appears to be important only in solvents of low polarity [15]. However, *C*-diazo coupling appears to be about twice as fast in water as in acetonitrile and this is probably due to change in solvation of the diazonium ion [13] [14]. Thus, if it is considered that either of the two theoretical lines in Figure 1 represents the normal coupling, the enhanced experimental rates above ca. 5% (v/v)  $\text{H}_2\text{O}$  may be due to a change in solvation of the diazonium ion.

However, the results in Table 1 suggest that another explanation is preferable. Thus, in *N*-coupling, DMSO is a more effective catalyst than pyridine, whereas in *C*-coupling the reverse is the case. In the comparison, the same or similar concentrations of additives in all three reactions were used, thus precluding an enhanced catalysis in a particular reaction by a di- or polymeric form of the additive. In water, DMSO ( $\text{p}K_a = -2.6$ ) [16a] is a weaker base than pyridine ( $\text{p}K_a = 5.24$ ) [16b], and the *C*-coupling reactions are expected to reflect greater the basicity of the catalyst (cf. *N*-coupling where H-bonding could play a (relatively) important role). The enhanced ability of DMSO in *N*-coupling is completely consistent with its ability to act as a stronger H-bond acceptor (Taft  $\beta$ -value = 0.752) than pyridine (Taft  $\beta$ -value = 0.661) [17].

It is known that amines form two types of H-bonds with water. That in which water acts as a H-bond donor  $\text{O}-\text{H} \cdots \text{N}$  is thought to be more important than that in which water acts as a H-bond acceptor  $\text{O} \cdots \text{H}-\text{N}$  [18]. It is expected that the second type of bond will facilitate electrophilic attack at amine N-atom by increasing the electron density at this atom; the stronger the H-bond acceptor, the greater the rate of reaction. Thus step 1, the formation of the  $\sigma$ -complex, should reflect, in general, the H-bond acceptor value of the solvent. This is supported by the enhanced rate at the (possible) limit in DMSO vs. water and perhaps by the strong catalysis shown by HMPT (Table 2).

In the case of water, the possibility that a change in structure could occur at these high concentrations must be considered. Thus in the flickering cluster model of Frank & Wen [19] it is proposed that the acidity of H in molecule a and the



basicity of O in molecule b is enhanced. There is little evidence for the former, but enhanced H-bonding basicity definitely occurs with increasing water structure [20]. A similar situation has been reported for alcohols [17].

Making the assumption that above 5% (v/v) water a change in structure occurs, then with increasing water content there will be a shift in equilibrium of H-bonded

complexes of the amine with water towards those involving the more basic water species. This will lead to an increase in the rate of step 1. However, both this effect and possible change in diazonium ion solvation should not lead to a change in  $k_2/k_{-1}$ . Although the experimental rate could be greater than that predicted from the  $S_E2$  mechanism because of these effects on  $k_1$ , there should still be a (slight) increase in rate at high (30%, v/v) water content, but this is not the case. It is thus necessary to assume that this proposed structure change in water also affects the  $k_2/k_{-1}$  value. The most obvious effect would be on  $k_2$ . Thus *Arnett et al.* have found that bulk water has about twice as large an H-bond acceptor effect as does monomeric water towards pyridinium ions and twice as strong an H-bond donor effect towards pyridines [21]. In the present case this should lead to an increase in the N, H-bond stretch in the  $\sigma$ -complex (H-acceptor effect) and possibly increased stabilization of the incipient diazoamino compound (H-donor effect). It is necessary to assume the change in  $k_{-1}$  is less; then  $k_2/k_{-1}$  will increase, which is equivalent to changing from the lowest to the middle theoretical line in *Figure 1*. This will again lead to an increase in rate not predicted by the  $S_E2$  mechanism.

There are thus three possible effects which can lead to the increased experimental rate, namely

- a) change in solvation of the diazonium ion;
- b) an increase in  $Kk_1$  with increased water structure;
- c) an increase in  $k_2/k_{-1}$  with increased water structure.

None of these effects is likely to be large, however it is only necessary to account for a difference of *ca.* 20% (*Fig. 1*). Concerning b) and c) as *Figure 2* shows, there is a change in slope of the plot of  $1/k_{\text{obs}}$  against  $1/[\text{H}_2\text{O}]$  at low water concentration; this is consistent with an increase in  $Kk_1$  and/or  $k_2/k_{-1}$  with increasing water concentration.

Concerning the catalysis shown by *t*-butylammonium chloride (*Table 3*), this may be due to increased  $Kk_1$  via stronger H-bonded species of the amine with  $\text{Cl}^-$  or perhaps due to an increase in water structure by added salt. However, the large rates observed with this additive in acetonitrile/DMF (*Table 3*) and in acetonitrile (*Table 2*) may be indicative of a concerted reaction. A similar situation could prevail with HMPT.

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### Experimental Part

**Materials.** - Amines were sublimed or distilled and diazonium salts prepared by the standard method [22] and recrystallized from dry acetonitrile/ether. Solvents were dried by standard methods and distilled. Acetonitrile had  $\text{N}_2$  bubbled through for 12 h and was then distilled under  $\text{N}_2$  ( $2 \times \text{P}_2\text{O}_5$ ,  $1 \times \text{K}_2\text{CO}_3$ ,  $1 \times$  alone). *t*-Butylammonium chloride was synthesized by the method described by *Brändström* [23] and recrystallized from ethyl acetate. It was stored in a dry box. (*N,N*- $2\text{H}_2$ )-*p*-Chloroaniline was prepared by  $\text{D}_2\text{O}$  exchange of the amine hydrochloride, and sublimed. 4,4'-Dichloro-diazoaminobenzene was prepared by the standard method [24] and purified by chromatography (neutral alumina;  $\text{C}_6\text{H}_6$ ) and recrystallization from petroleum ether (60-90°).

**Kinetics.** - The dry solvent was transferred to the N<sub>2</sub> dry box (*Vacuum/Atmosphere Corporation*) without exposure to air and used to prepare a  $5 \times 10^{-5}$ M solution of the diazonium salt. Aliquots (3 ml) were added to spectrophotometer cells which were transferred to a spectrophotometer thermostated at 30°. Samples of amine and additive were added by syringe to start the reaction, and the increase in absorbance of the product was followed with time. For experiments carried out with percentages of additive above 5% (v/v), the solvent mixture was prepared in air over a stream of dry N<sub>2</sub>.

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