162. Mechanisms of Diazo Coupling Reactions. Part XXXI. Aminoazo Formation in the Diazo Coupling of *N,N*-Dimethylaniline and *m*-Toluidine with *p*-Methoxybenzenediazonium Tetrafluoroborate in Acetonitrile[1])

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Summary

In the title reactions it is shown that aminoazo formation does not occur by direct attack of diazonium ion at C-atom. Initial attack is at N-atom, but proton loss from the σ_N-complex formed is relatively slow. Hence, at low amine concentration this rearranges intermolecularly to the aminoazo derivative. At high amine concentration a second method of aminoazo formation can take place involving attack of an amine molecule on the σ_N-complex or on a molecular complex formed between the diazonium ion and the amine. Implication of these proposals for the diazoamino rearrangement are discussed.

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1. Introduction. - It has been reported in [2] that primary aromatic amines usually form diazoamino compounds in coupling with benzenediazonium salts (*N*-coupling) except when the nucleophilic reactivity of the aryl residue is raised by substituents or fused rings as in *m*-toluidine and 1- and 2-naphthylamine when aminoazo formation takes place (*C*-coupling). However, the possibility has also been noted that in aminoazo formation, initial attack of the diazonium may still be at amine N-atom, but the decomposition of the σ_N-complex might well be too rapid to allow its identification [3].

In a recent communication [4] we reported this could indeed be the case. The coupling reactions of *m*-toluidine (MT) and *N,N*-dimethylaniline (DMA) with *p*-methoxybenzenediazonium tetrafluoroborate in dry acetonitrile showed a number of unusual characteristics, in particular an increase in kinetic hydrogen isotope effect with temperature. Majority *C*-coupling occurs ($\geqslant 86\%$ for MT, $\geqslant 92\%$ for DMA), but on addition of a *t*-alkylammonium chloride, a large increase in rate takes place and majority diazoamino compounds (with loss of a methyl group for DMA) are formed. This led us to conclude that initial attack of the diazonium ion is at amine N-atom and aminoazo formation occurs *via* rearrangement. However, the data were not consistent with a simple intermolecular rearrangement of the σ_N-complex. Work on the diazoamino rearrangement of substituted *N*-methyl-

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[1]) Part XXX, see [1].

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diazoamino compounds in ethanol/water 95:5 led us to suppose that the rate-limiting step in the rearrangement was fission of the σ_N-complex to the diazonium ion and amine. As this was much slower than aminoazo formation it was necessary to postulate that rearrangement took place *via* a species which occurred earlier than the σ_N-complex on the reaction pathway, namely a molecular complex. The data were not consistent with the sole operation of this pathway. At high amine concentration we proposed that aminoazo formation could also occur by attack of an amine molecule on the complex.

It now appears, however, that, under our conditions, the rate-determining step in the diazoamino rearrangement of 4′-methoxy-3-methyl-diazoaminobenzene could be protonation [1]. If so, the σ_N-complex could be involved in the formation of aminoazo compounds in the coupling reactions, and a reevaluation of the situation is necessary.

We report here previously unpublished data, principally for MT, but also for DMA together with our interpretation of the unusual characteristics exhibited by these reactions.

2. Results. - Our preliminary observations of the two coupling reactions were carried out in dry acetonitrile in air. Rate constants were measured by following the increase in absorbance of the products with time, but were not easily reproducible, particularly at low amine concentration. Solvent from several manufacturers and purified by several different methods gave essentially the same results, and the non-reproducibility was eventually traced to small amounts of water picked up by the dry solvent from the atmosphere during handling operations. When solutions were prepared in a nitrogen dry box, good reproducibility was obtained. To standardize the conditions, the solvent was deoxygenated before distillation and drying under nitrogen.

The reactions were studied at three temperatures (12.9°, 31.1°, 47.2°) and seven amine concentrations (0.004–0.256 M). In all experiments the concentration of the diazonium salt was 5×10^{-5} M. With DMA, there was very little effect of amine concentration or temperature on the infinity spectrum of the product ($\lambda_{max} = 408$ nm at 31.1°). With MT, however, there was a small, but definite shift to shorter wavelengths with increasing amine concentration, for example at 31.1° λ_{max} decreased from 391 nm to 388 nm on changing the concentration from 0.032 M to 0.256 M. Further, the product formed from the deuteriated amine had, in general a λ_{max} about 1–2 nm lower than of the undeuteriated amine. In general, the infinity values were stable, but particularly at low amine concentration and the highest temperature a gradual increase was observed for MT. These observations were traced to the fact that not only the aminoazo, but also the diazoamino compound was formed with MT. Thus addition of the latter to an infinity solution showed that it decomposed at exactly the same (relatively slow) rate as the infinity solution itself. Test mixtures of diazoamino and aminoazo compounds showed that not more than 20% of the former was formed, and it was possible to calculate the concentration of the aminoazo derivative at 430 nm. The change in this concentration is shown in *Table 1*. We claim no great accuracy for these changes, but a definite decrease in aminoazo concentration with increasing amine concentration is

Table 1. *Change in yield of aminoazo compound with amine concentration and temperature for the coupling of* m-*toluidine*[a])

[Amine] (mol l^{-1})	12.9°	31.1°	47.2°
0.004	100.0 (100.0)[b])	100.0 (100.0)	100.0 (100.0)
0.008	100.0 (100.0)	100.0 (100.0)	100.0 (100.0)
0.016	100.0 (100.0)	100.0 (100.0)	100.0 (100.0)
0.032	91.4 (87.2)	92.7 (88.6)	97.0 (92.8)
0.064	92.5 (88.9)	91.5 (86.8)	93.1 (89.0)
0.128	90.7 (88.7)	90.0 (84.7)	88.0 (84.7)
0.256	86.5 (85.5)	86.1 (82.5)	86.8 (82.5)

a) Estimated error ±5% of value shown. Measured at 430 nm. Values for [2,4,6-$^2H_3$]-*m*-toluidine are in brackets.

b) All values of 100% are assumed.

observable. Unfortunately, attempts to isolate the diazoamino compound from infinity solutions by chromatography failed; with every method used it decomposed.

Because of the difficulty in obtaining accurate values of the infinity at low amine concentration, rate constants were measured only for the four highest concentrations. In general, three measurements were made for each particular concentration and temperature, and agreement was within 5%. Below 0.032 M, the initial slope method was used. During a run there was no change in λ_{max} with time and agreement between rate constants and rates measured by the initial slope method

Table 2. *Change in order with respect to amine concentration* (n_A) *and kinetic hydrogen isotope effect* (k_H/k_D) *with amine concentration and temperature in the coupling of* m-*toluidine*[a])

[Amine] (mol. l^{-1})	12.9°		31.1°		47.2°	
	n_A[b])	k_H/k_D[b])	n_A	k_H/k_D	n_A	k_H/k_D
0.004		2.06		1.99		1.95
	1.75		1.83		1.81	
0.008	(1.78)		(1.86)		(1.85)	
		2.01		1.95		1.90
	1.83		1.91		1.95	
0.016	(2.02)		(1.90)		(1.93)	
		1.77		1.97		1.92
	1.59		1.70		1.73	
0.032	(1.67)		(1.80)		(1.76)	
		1.63		1.88		2.20
	1.27		1.49		1.65	
0.064	(1.54)		(1.60)		(1.89)	
		1.35		1.75		1.86
	1.29		1.38		1.49	
0.128	(1.44)		(1.66)		(1.77)	
		1.22		1.45		1.54
	1.25		1.34		1.55	
0.256	(1.48)		(1.61)		(1.75)	
		1.04		1.21		1.34

a) For aminoazo formation. Values for [2,4,6-$^2H_3$]-*m*-toluidine are in brackets.

b) Estimated error ±5% of value shown.

Table 3. *Change in activation parameters with amine concentration and temperature in the coupling of* m-*toluidine*a)

[Amine] (mol. l^{-1})	12.9-31.1° $\Delta H^{\neq}$ b)	$\Delta S^{\neq}$ c)	31.1-47.2° $\Delta H^{\neq}$	$\Delta S^{\neq}$ d)
0.004	25.2	− 173	22.9	− 175
	(26.4)	(− 174)	(24.2)	(− 170)
0.008	27.3	− 167	22.9	− 177
	(28.5)	(− 171)	(23.8)	(− 177)
0.016	29.4	− 158	23.4	− 172
	(25.6)	(− 167)	(25.0)	(− 172)
0.032	33.4	− 150	27.0	− 167
	(27.7)	(− 172)	(19.1)	(− 198)
0.064e)	39.6	− 137	32.3	− 153
	(29.3)	(− 170)	(29.2)	(− 162)
0.128	42.0	− 129	36.7	− 145
	(35.0)	(− 152)	(33.3)	(− 153)
0.256	44.3	− 121	43.3	− 122
	(38.8)	(− 140)	(38.2)	(− 138)

a) For aminoazo formation. Values for [2,4,6-$^2H_3$]-*m*-toluidine are in brackets.

b) kJ mol^{-1}. Estimated error ± 2.5 kJ mol^{-1}.

c) J mol^{-1} per degree. Estimated error ± 10 J mol^{-1} per degree. At 12.9°.

d) At 47.2°.

e) These values are not altered when reaction is carried out in the presence of 2.0 × 10^{-5}M 4′-methoxy-3-methyl-diazoaminobenzene.

was good. The rate constants so obtained were corrected for the change in aminoazo concentration and used to calculate the order with respect to amine concentration (n_A), the kinetic isotope effect (k_H/k_D), $\Delta H^{\neq}$ and $\Delta S^{\neq}$. These are shown in *Tables 2* and *3*. As with DMA [4], definite trends are observable. *Table 2* shows that, at a particular temperature, with increasing amine concentration, n_A and k_H/k_D decrease except at low concentration where constancy is achieved. It was not possible to study the reaction at a concentration higher than 0.256M, but with DMA at 5°, n_A achieves a constant value of *ca.* 1.1 between 0.121 and 1.01M amine.

At a particular amine concentration, an increase in temperature increases n_A and k_H/k_D, but at low concentration there is little effect. Values for the deuteriated

Table 4. *The effect of addition of* t-*butylammonium salts on the coupling of* N,N-*dimethylaniline at 31.1°*

[Amine] (mol. l^{-1})	k_{obs} (s^{-1})a)	[Anion] of salt (mol. l^{-1})
0.064	1.46 × 10^{-3}	-
	7.00 × 10^{-3}	0.016 Cl^-
	1.40 × 10^{-2}	0.032 Cl^-
	2.80 × 10^{-2}	0.064 Cl^-
0.256	7.20 × 10^{-3}	-
	6.77 × 10^{-3}	0.01 BF_4^-
	7.40 × 10^{-3}	0.01 HSO_4^-
	7.62 × 10^{-3}	0.01 Br^-

a) Pseudo first-order rate constant.

Table 5. *The effect of the addition of* t-*butylammonium chloride on the coupling of* m-*toluidine* (0.128 M) *at 31.1°*

k_{obs} (s^{-1})[a])	[salt] (mol. l^{-1})	%DA[b])	%AA[c])
5.53×10^{-3}	-	9	91
8.00×10^{-2}	0.0014	79	21

a) Pseudo first-order rate constant b) Diazoamino compound. c) Aminoazo compound.

amine show the same trends, but here n_A is greater although the values for the two amines approach each other at low amine concentration.

This apparent constancy of the n_A and k_H/k_D values at low concentration is reflected in the activation parameters shown in *Table 3.* Here, however, at a particular temperature ΔH^{+} and ΔS^{+} increase with increasing amine concentration, but decrease with temperature at a particular concentration. Addition of 2.0×10^{-5} M diazoamino compound at the beginning of a run has very little effect on ΔH^{+} and ΔS^{+}. Again, the deuteriated amine shows the same trend, but has ΔH^{+} and ΔS^{+} values lower than for the undeuteriated amine.

In order to investigate the possible importance of a diazonium salt ion pair equilibrium we studied the effect of salts on the reaction with DMA *(Table 4).* With the BF_4^- salt, a small decrease in rate is observed, but slight increases with the HSO_4^- and Br^- salts are found. In contrast, large increases in rate are found with Cl^- and there is a 60 nm shift in product spectrum to lower wavelengths. The infinity spectrum corresponds to that of 4-methoxy-*N*-methyldiazoaminobenzene.

A similar situation is found with MT. A representative example is given in *Table 5.* Cl^- brings about a large increase in rate and a change in product proportion from 10% to *ca.* 80% diazoamino compound. This effect is not peculiar to Cl^-. Thus water also acts in this manner. Indeed, with water, addition of *ca.* 25% (*v/v*) produces a rate increase of *ca.* 100, and a change in product to 90% diazoamino with 0.005 M MT. Above this percentage water, there is very little change in rate. The situation is analogous to that found for *p*-chloroaniline [1].

In the case of MT we have also measured the reverse reaction, the acid-catalyzed decomposition of 4′-methoxy-3-methyldiazoaminobenzene. The reaction is first-order in diazoamino compound, first-order in 3-methylanilinium tetrafluoroborate and has order *ca.* −0.2 in amine. At 47.2° it is 450× slower than the coupling

Table 6. *Relative coupling rates of* p-*chloroaniline,* N,N-*dimethylaniline, aniline and* N-*methylaniline with* p-*chlorobenzenediazonium tetrafluoroborate in* H_2O/*acetonitrile 30:70* (v/v) *at 30°*

Amine	Relative rate	Product
p-Chloroaniline[a])	1	DA[b])
DMA[c])	2.2	AA
Aniline[d])	5.4	DA
NMA[e])	106.1	DA

a) At 355 nm. b) DA = diazoamino; AA = aminoazo. c) At 417 nm. d) At 350 nm. e) At 333 nm.

reaction at 0.256 M MT and only approaches the rate of this at the lowest concentration where the rates are approximately the same.

Finally, we have measured the relative rates of MT, DMA, aniline and *N*-methylaniline (with the *p*-chlorobenzenediazonium salt) in acetonitrile containing 30% (*v*/*v*) water. As *Table 6* shows DMA forms the aminoazo compound, but is over 50× less reactive than *N*-methylaniline.

3. Discussion.

– It is convenient to begin the discussion with a summary of the results presented in *Tables 2* and *3* and to a much lesser extent in [4]. In general both DMA and MT reactions show the same trends, and it is our intention only to draw attention to the general characteristics of these reactions and not to concentrate on small changes.

	At low concentration of amine	*At high concentration of amine [4]*	*At intermediate concentration of amine*	
			Constant T, increase in amine concentration	*Constant amine concentration, increase in T*
k_H/k_D	constant: *ca.* 2.0	constant: $\leqslant 1$	decreases	increases
n_A	constant: *ca.* 1.9	constant: *ca.* 1	decreases	increases
$\Delta H^{\ddagger}, \Delta S^{\ddagger}$	constant: low	constant: high	increase	decrease

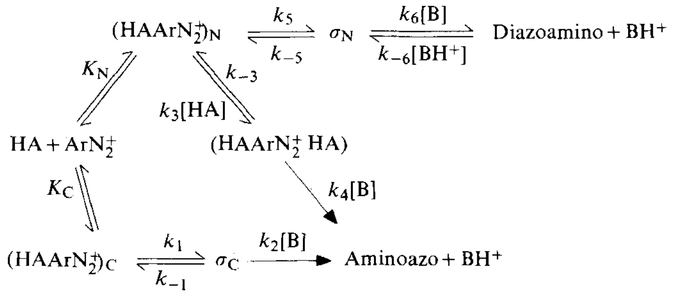
Finally, we note that at intermediate amine concentration the deuteriated amines have higher n_A and lower $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

To simplify matters it is instructive to consider the relationship between the various parameters. The observation that the deuteriated amines have lower $\Delta H^{\ddagger}$ will automatically lead to an increase in k_H/k_D with temperature as the reaction with the higher $\Delta H^{\ddagger}$ will show a greater increase in rate at the higher temperature. Further, considering the increase in n_A with temperature, n_A is given by the slope of a plot of $\ln k_{obs}$ against $\ln[\text{amine}]$. At low amine concentration $\Delta H^{\ddagger}$ is low, whereas at high amine concentration $\Delta H^{\ddagger}$ is high, thus any increase in temperature will automatically bring about an increase in slope and hence an increase in n_A. We are thus left to account for:

a) The change in product proportions with addition of base;
b) The change in n_A and k_H/k_D, with amine concentration;
c) The change in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with amine concentration and temperature;
d) The differences between the deuteriated and undeuteriated amines.

Considering point *a* first, our previous work [1] has shown that the *N*-coupling of *p*-chloroaniline with *p*-chlorobenzenediazonium tetrafluoroborate in acetonitrile exhibits non-linear base catalysis on addition of water, and a limiting rate is reached with *ca.* 25% (*v*/*v*) water. This was interpreted in terms of base catalysis of rate-limiting proton loss in the S_E2 mechanism. We have observed exactly the same situation in the *N*-coupling of MT with *p*-methoxybenzenediazonium tetrafluoroborate and it is logical to conclude that a similar situation applies. Thus the first conclusion we can draw is that in the *C*-coupling of the two amines initial attack of the diazonium ion is at amine N-atom. If in the *Scheme* we ignore, for

Scheme



HA Aniline derivative
ArN$_2^+$ Diazonium salt
B Base
k_6[B], k_{-6}[BH$^+$] are small under our conditions.

the moment, the formation of complexes (HAArN$_2^+$)$_N$, (HAArN$_2^+$)$_C$ and (HAArN$_2^+$ HA) and consider that MT undergoes two parallel reactions namely *C*- and *N*-coupling both of which operate by the S_E2 mechanism then k_{obs} can be calculated from equation 1.

$$k_{obs} = \frac{k_1 k_2 [B]}{k_{-1} + k_2 [B]} + \frac{k_5 k_6 [B]}{k_{-5} + k_6 [B]} \tag{1}$$

The rate constant k_{-6} can be ignored as the acid-catalyzed decomposition of the diazoamino compound is relatively slow.

In the limits $k_2[B]/k_{-1}$ and $k_6[B]/k_{-5} \gg 1$

$$k_{obs} = k_1 + k_5 \tag{2}$$

Under this condition (in *ca.* H$_2$O/acetonitrile 25:75 (*v/v*)) we observe *ca.* 80–90% diazoamino formation, hence k_5 is 4 to 9 times larger than k_1, *i.e.* initial attack occurs principally at the N-atom. The observation of a limiting rate is thus important as it allows this unambiguous conclusion. It is supported by the data in *Table 6*. Thus *N*-methylaniline undergoes *N*-coupling *ca.* 20× faster than aniline, and it is difficult to believe that introduction of a second methyl group at the N-atom would so lower the rate for DMA that attack at C-atom is preferred. The fact that aminoazo compound is formed must be due to rearrangement. We note that if *N*-coupling were a concerted reaction, then initial attack of the diazonium ion in our reactions could, but need not necessarily, take place at amine N-atom.

It is clear, however, that our observations can not be explained in terms of a change in proportion of two parallel reactions. Although with MT there is an increase in proportion of diazoamino compound with amine concentration, this is not the case with DMA which shows similar characteristics. Thus we have to consider some form of rearrangement to account for formation of the aminoazo compounds. Although at low amine concentration the acid-catalyzed rearrangement of 4′-methoxy-3-methyldiazoaminobenzene is of comparable rate to *C*-coupling, at intermediate to high amine concentration this is not the case. Rearrangement thus involves the σ_N-complex or a species preceding this on the reaction pathway. We shall first consider the situation in terms of a mechanism involving a simple intermolecular rearrangement of the σ_N-complex without the involvement of any molecular complex.

Such a mechanism can account for a number of our observations. Thus we know from the change in product proportions with added base that $k_6/k_{-5} < k_2/k_{-1}$, *i.e.* the *C*-coupling reaction reaches a limiting rate at a much lower base concentration than *N*-coupling. Further, the proportion of diazoamino to aminoazo depends on competition between $k_6[B]$ and k_{-5} and hence should increase with increasing base, *i.e.* amine concentration. As *Table 1* shows this is the case. The rate constant for aminoazo formation is given by equation 3.

$$k_{\mathrm{obs}} = \frac{k_{-5}}{k_5 + k_{-5}} \; \frac{k_1 k_2 [\mathrm{B}]}{k_{-1} + k_2 [\mathrm{B}]} \tag{3}$$

In the limit at low amine concentration when $k_5 < k_{-5}$ then equation 4 has to be applied.

$$k_{\mathrm{obs}} = \frac{k_1 k_2 [\mathrm{B}]}{k_{-1} + k_2 [\mathrm{B}]} \tag{4}$$

The reaction should show characteristics typical of a normal *C*-coupling, *i.e.* $k_H/k_D > 1$ and $n_A = 2$. This is the case with MT. Further, kinetic isotope effects are thought to arise in the S_E2 mechanism because $k_{2H} > k_{2D}$, *i.e.* $\Delta H^{\ddagger}_{H} < \Delta H^{\ddagger}_{D}$ and, again, this is the case with MT at low amine concentration. Although the differences are well within experimental error, they are consistent with the general trend that $\Delta H^{\ddagger}_{H}$ and $\Delta H^{\ddagger}_{D}$ approach each other at high and low amine concentration.

At low amine concentration, however, the activation enthalpies (and entropies) appear very low for a *C*-coupling. A direct comparison with literature data is not possible, but under aqueous conditions a normal value for ΔH^{+} would appear to be *ca.* 59 kJ mol^{-1} (14 kcal mol^{-1}) [3] [5]. In our opinion it is necessary to provide an explanation for this low value of ΔH^{+} and ΔS^{+} and particularly for the change in ΔH^{+} and ΔS^{+} with amine concentration. There are several possibilities, but the most obvious involves molecular complex formation between the diazonium ion and the amine.

In recent years, evidence has been presented to show that such complexes are formed in aqueous [6] and non-aqueous (see *e.g.* [7]) solvents in diazo coupling and that they lie on the reaction pathway. In the *Scheme* we show two orientated molecular complexes at C- and N-atom. In all probability, a non-oriented complex is first formed, but is excluded for reasons of simplicity. The following argument would be essentially the same if such a complex were included. The observed rate constant for aminoazo formation *via* rearrangement is now given by equation 5.

$$k_{\mathrm{obs}} = \frac{1}{1 + K_{\mathrm{N}}[\mathrm{HA}]} \; \frac{K_{\mathrm{C}}[\mathrm{HA}]}{1 + K_{\mathrm{C}}[\mathrm{HA}]} \; \frac{k_{-5}}{k_5 + k_{-5}} \; \frac{k_1 k_2 [\mathrm{B}]}{k_{-1} + k_2 [\mathrm{B}]} \tag{5}$$

At low [HA], $1 > K_N[HA]$, $K_C[HA]$; $k_5 < k_{-5}$; $1 > k_2[B]/k_{-1}$ hence k_{obs} and $\Delta H^{\neq}$ are given by equation 6 and 7, respectively

$$k_{obs} = K_C \frac{k_1 k_2 [B]}{k_{-1}} \tag{6}$$

$$\Delta H^{\neq} = \Delta H_C^\circ + \Delta H_1^{\neq} + \Delta H_2^{\neq} - \Delta H_{-1}^{\neq} \tag{7}$$

It is immediately obvious that if ΔH_C° is negative a low activation enthalpy will result. Similarly, with $\Delta S^{\neq}$. There is ample evidence to suggest this is the case (see *e.g.* [7]) and a value of *ca.* -21 kJ mol^{-1} (-5 kcal mol^{-1}) for ΔH_C° in the present case is not unreasonable if one assumes a 'normal' activation enthalpy of *ca.* 45 kJ mol^{-1} (11 kcal mol^{-1}).

The postulation of complex formation also provides an explanation for the change in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with [HA] and temperature if it is assumed that $K_N[HA]$ in the above equation becomes > 1 at high [HA] (and calculations show this is perfectly feasible under our conditions). We obtain equation 8 for k_5 at high [HA].

$$k_{obs} = \frac{1}{K_{N[HA]}} \frac{K_C[HA]}{1 + K_C[HA]} \frac{k_{-5}}{k_5 + k_{-5}} k_1 \tag{8}$$

There is now a positive contribution from $\Delta H_N^\circ(\Delta S_N^\circ)$ to the total activation enthalpy (entropy). Here we have considered only that $K_N[HA] > 1$ at high [HA]. Possibly $K_C[HA] > 1$ also holds, but this only reinforces the argument. Further, we would not consider such a large change to occur in the value of $k_{-5}/(k_{-5} + k_5)$. Thus, the susceptibility of *N*-coupling to base catalysis and the fact that protonated diazoamino compounds have never, to our knowledge, been observed point to the fact that k_{-5} is large, hence, writing the above as an equilibrium, *i.e.* $1/(1 + K_5)$, we do not expect a large change in the contribution of this step with change in [HA] ($1/K_5$ at high [HA]) to the total.

Thus at high [HA] we expect a larger $\Delta H^{\neq}$ (and $\Delta S^{\neq}$) and further a return to a more normal temperature effect on the activation parameters. Our earlier work with DMA has shown this is indeed the case [4]. However, the required change necessitates that at high [HA], the reaction is independent of [HA] (or possibly $n_A = -1$ if $K_C[HA]$ is > 1). This is definitely not the case.

For DMA up to *ca.* 1 M [HA], n_A is constant, and approximately equal to 1.0. There is no indication of an order lower than one. This led us to postulate that a second reaction occurs which involves attack of a molecule of amine on the *N*-oriented molecular complex *(Scheme)*. In this case k_{obs} is given by equation 9

$$k_{obs} = \frac{1}{1 + K_C[HA]} \frac{K_N[HA]}{1 + K_N[HA]} \frac{k_3[HA]k_4[B]}{k_{-3} + k_4[B]} \tag{9}$$

and at high [HA], $1 < K_N[\mathrm{HA}]$; $1 < K_C[\mathrm{HA}]$; $1 < k_4[\mathrm{B}]/k_{-3}$ equation 10 is obtained,

$$k_{\mathrm{obs}} = k_3[\mathrm{HA}] \tag{10}$$

which accounts for the observed change in n_A with [HA]. We envisage that at low [HA] only intermolecular rearrangement occurs *via* σ_N. With increasing [HA], however, the second reaction will incur because of greater n_A (and because the intermolecular rearrangement is retarded by increased K_N). This reaction predominates at high [HA]. There is some precedent for this in the literature. Thus in the reaction of DMA with tetracyanoethylene in chloroform, *Rappoport* [9] found it necessary to postulate that a second molecule of DMA attacks a 1:1 molecular complex formed between the amine and tetracyanoethylene.

Our conclusion that *N*-coupling occurs by the S_E2 mechanism with rate-limiting proton transfer does not allow the unambiguous conclusion that it is the molecular complex which undergoes attack by a molecule of amine in this second reaction. From the principle of microscopic reversibility, the rate-determining step in the diazoamino rearrangement of 4′-methoxy-3-methyldiazoaminobenzene is protonation under our conditions. Hence, it is also possible that the σ_N-complex is attacked by amine.

Clearly, in the diazoamino rearrangement, if protonation is rate-determining, attack by amine on either σ_N-complex or the molecular complex will not be detectable. If decomposition of the protonated diazoamino compound is rate-determining then attack on σ_N should be detectable, but attack on the molecular complex will not. This may explain why, in only a few cases, has such a reaction been observed, but yields of aminoazo are always better in pure amine solvent. This would depend on competition between reaction yielding aminoazo and reactions leading to decomposition of an intermediate or the diazonium salt, but which occur after the rate-limiting step.

Concerning the final point, the differences which exist between the deuteriated and undeuteriated amines in n_A, ΔH^{+} and ΔS^{+} at intermediate amine concentration, again several possibilities exist, but it is only necessary to assume that the deuteriated amines undergo more of the reaction involving amine attack on the molecular complex or σ_N-complex. The observation of an inverse kinetic isotope effect at high amine concentration lends support to this view.

Finally, we should like to stress that while our deductions provide a reasonable explanation for the observations, other interpretations could be possible, but in the absence of more data we prefer not to commit ourselves further.

The most important general result of this and the preceeding investigations [1] [4] is the fact that the experimental results are not explainable by *one* mechanism of diazoamino rearrangement, but by *two* mechanisms namely by a competitive complete back reaction from the diazoamino compound to the amine and the diazonium ion, and an attack of amine on the molecular complex $(\mathrm{HAArN_2^+})_N$.

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4. Experimental Part. - *Materials.* Amines were dried and distilled. The purification of the solvent and the preparation of the diazonium salt and *t*-butylammonium chloride have been described [1]. Other salts were used without purification. [2,4,6-$^2H_3$]-Amines were prepared by five D_2O exchanges (10× ex., 24 h) of the hydrochlorides at 100°. After basification with Na_2CO_3 the amines were washed, dried and distilled. MS. showed >98% deuteriation. The 4′-methoxy-4-aminoazobenzene derivatives were prepared by reaction of 1 M solutions of the diazonium salt and the amine in acetonitrile for 24 h at room temperature. The tetrafluoroborates of the dyes formed were isolated, basified and the free bases filtered off, washed with water and dried. The dyes were recrystallized twice from ethanol. 4′-Methoxy-3-methyldiazoaminobenzene was initially prepared by reaction of 1 M solutions of the diazonium salt and amine in acetonitrile/pyridine 1:1. The reaction mixture was poured into water, the solid filtered off, washed with water and dried. It was purified by column chromatography on neutral alumina with eluent benzene and recrystallized twice from petroleum ether (60-90°). A later method employed water/acetonitrile 30:70 (*v*/*v*) as solvent which gave better yields.

Kinetics. The procedure has been described previously [1].

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