Diazo Coupling Reactions in Acetonitrile: an Apparent Increase in Kinetic Isotope Effect with Temperature[1]

By John R. Penton and Heinrich Zollinger*

(Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule Zürich, Universitätstrasse 6, CH-8092 Zürich, Switzerland)

Summary The increase in kinetic isotope effect with temperature in diazo coupling reactions of NN-dimethylaniline and 3-methylaniline is attributed to partitioning of aminoazobenzene formation between two reactions, both of which involve molecular complex formation between the diazonium salt and amine nitrogen.

KINETIC isotope effects normally decrease with increasing temperature. We report here reactions, viz. the diazo coupling of 4-methoxybenzenediazonium tetrafluoroborate with 3-methylaniline (1) and NN-dimethylaniline (2) in anhydrous acetonitrile under nitrogen at 285·9, 304·1, and 320·2 K, which appear to show the opposite. For both amines (HA), the major product is the 4'-methoxy-4-aminoazobenzene derivative [$\geqslant 79\%$ for (1), $\geqslant 92\%$ for (2)]. Representative data for (2) are in the Table.

An increase in temperature increases k_H/k_D and n_{HA}, and decreases $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Conversely, at a particular

TABLE. Diazo coupling of NN-dimethylaniline with 4-methoxybenzenediazonium tetrafluoroborate.

Temp./K	285·9			285·9—304·1	320·2			304·1—320·2	320·2		304·1—320·2
[HA]^a	k_H/k_D^b	n_{HA}^c	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	k_H/k_D	n_{HA}	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	n_{HA}	$\Delta S^{\ddagger\ddagger}$	$\Delta H^{\ddagger\ddagger}$
0·256	0·86		−97	56·5	1·05		−89	59·0		−101	54·4
		1·05				1·21			1·39		
0·128	0·96		−101	56·1	1·19		−103	54·0		−120	47·7
		0·95				1·19			1·44		
0·064	1·02		−106	52·3	1·41		−108	50·6		−134	42·7
		1·10				1·43			1·55		
0·032	1·14		−115	49·0	1·54		−127	43·5		−145	37·2
		1·33				1·59			1·75		
0·016	1·38		−123	45·6	1·80		−135	39·3		−151	32·6
		1·54				1·82			2·01		
0·008	1·53		−137	41·4	2·05		−147	34·3		−170	27·2
		1·57				1·81			1·90		
0·004	1·69		−141	38·1	2·20		−159	30·5		−185	23·0

^a In mol dm^{-3}; [diazonium salt] = 5×10^{-5} mol dm^{-3} in all cases. ^b Kinetic isotope effect with NN-dimethyl[2,4,6-$^2H_3$]aniline. Estimated error $\pm5\%$. ^c Order with respect to [HA]. Estimated error: $\pm5\%$. ^d In J mol^{-1} k^{-1}. Estimated error: ±10 J mol^{-1} K^{-1}. ^e In kJ mol^{-1}. Estimated error: $\pm$ 2·5 kJ mol^{-1}. ^f For NN-dimethyl[2,4,6-$^2H_3$]aniline.

temperature, an increase in [HA] decreases k_H/k_D and n_{HA}, but increases $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The deuteriated amine has higher n_{HA}, and lower $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The data for (1) show the same trends, but at low [HA] ($\leqslant 0·008$ mol dm^{-3}) the values depend only slightly on [HA], and there is little difference between the undeuteriated and deuteriated amines. In particular, n_{HA} approaches 2.

The decrease in k_H/k_D and n_{HA} with increasing [HA] is expected from the well established mechanism of diazo coupling,[2] but the temperature effects are anomalous. However, the lower $\Delta H^{\ddagger}$ of the deuteriated amines is responsible for the increase in k_H/k_D with temperature and the increase in n_{HA} can be attributed to the increase in $\Delta H^{\ddagger}$ with [HA]. The effect of [HA] and temperature on $\Delta H^{\ddagger}$ (and $\Delta S^{\ddagger}$) is consistent with an S_E2 reaction involving initial formation of a molecular complex,[3] but there are complications in the present cases.

Such a mechanism requires that the rate be independent of [HA] at high [HA],[3,4] whereas a first-order dependence is observed.† Further, addition of the strong base $Me_4N^+Cl^-$ increases the reaction rates and $\geqslant 90\%$ of diazoamino compounds are formed [with loss of N-methyl from (2)]. This implies that, in the absence of base, initial attack of the diazonium ion is at nitrogen, loss of proton or methyl cation from σ_N (Scheme) is slow, and aminoazo compounds are formed by rearrangement. Experimentally, however, for (1) at high [HA] (0·256 mol dm^{-3}) the rate-limiting step in the diazoamino rearrangement is step 5, and is not attack of HA on σ_N (unpublished work).

To account for these observations we propose that aminoazo compounds are formed by two reactions, both of which involve initial formation of a molecular complex $(HAS)_N$ between the diazonium ion and amine nitrogen. The rate is given by expressions (1) + (2). Under the

$$[S] \; \frac{1}{1 + K_N[HA]} \; \frac{K_C[HA]}{1 + K_C[HA]} \; \frac{k_1 k_2 [B]}{k_{-1} + k_2 \, [B]} \qquad (1)$$

$$[S] \; \frac{1}{1 + K_C[HA]} \; \frac{K_N[HA]}{1 + K_N[HA]} \; \frac{k_3 [HA] k_4 [B]}{k_{-3} + k_4 [B]} \qquad (2)$$

present conditions $K_N \gg K_C$, B = HA, and $[HA]_0 \gg [S]_0$. At low [HA], $(HAS)_N$ rearranges intermolecularly [reaction (1)] via HA and S, and reaction (2), attack of HA on the complex, is negligible. With increasing [HA], reaction (2) is favoured by virtue of its higher n_{HA} and the increase in $K_N[HA]$, and is predominant at high [HA].

high [HA]: rate = [S] $k_3[HA]$
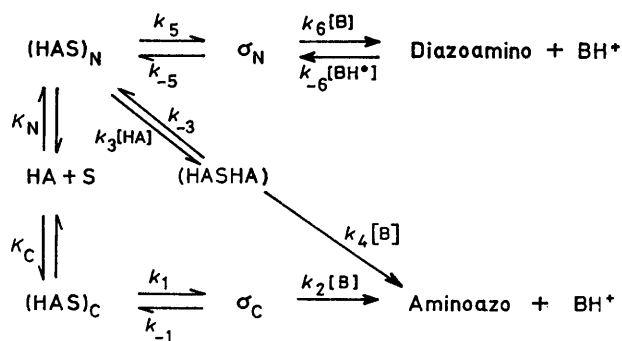$K_N[HA] \gg 1 \gg K_C[HA]$
$k_4[HA]/k_{-3} \gg 1$

low [HA]: rate = [S] $K_C \, k_1 k_2 [HA]^2/k_{-1}$
$1 \gg K_N[HA] \gg K_C[HA]$
$1 \gg k_2[HA]/k_{-1}$

To account for the lower $\Delta H^{\ddagger}$ (and lower $\Delta S^{\ddagger}$ and higher n_{HA}) shown by the deuteriated amines, we suggest that, at intermediate [HA] values, these amines react more by reaction (2). This view is supported by the observation of an inverse k_H/k_D at high [HA].

SCHEME. HA = aniline derivative; S = diazonium salt; B = base; k_5, k_{-5}, and $k_6[B]$ are slow enough to be ignored.

The Scheme is intended only to illustrate the essential characteristics of the reactions. The present data do not

† This was carefully checked at [HA] higher than those in the Table.

allow unambiguous identification of the nature of the two mechanisms, and other possibilities exist, *e.g.* at low [HA] the data are consistent with intramolecular rearrangement of $(HAS)_N$. Investigation of these mechanisms is in progress, in particular the catalysis of diazoamino formation by tetra-alkylammonium salts.

[1] 29th Communication on the mechanism of diazo coupling reactions. 28th Communication: S. B. Hanna, C. Jermini, H. Loewen-schuss, and H. Zollinger, *J. Amer. Chem. Soc.*, 1974, **96**, 7222.
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