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VOLUMES OF ACTIVATION FOR ANION-DIAZONIUM ION RECOMBINATION

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Anion-cation recombination reactions between aryldiazonium ions and anionic nucleophiles have volumes of activation which are small or even negative against expectations of considerably positive values resulting from release of electrostricted solvent. Various interpretations of these results are considered.

It is well established that ionogenic processes are characterised by negative volumes of activation,accounted for by the increasing solvation around the developing charge centres [1a-c]. Conversely,ion recombination reactions should have positive volumes of activation and of reaction by reason of solvent relaxation as charges become neutralised. This is the case for displacements of 'onium leaving groups by anionic nucleophiles in S_N2 reactions [2]. We have previously shown,however, that exceptionally, a recombination reaction may have a negative volume of activation,e.g. reactions of cations of the triphenylmethyl dyes with anionic nucleophiles .In a wide variety of solvents these processes show negative volumes of activation although they have positive volumes of reaction.

$Ar_3C^+ + Nu^- \longrightarrow Ar_3C\text{-}Nu; \Delta V^{\neq} = -4$ to $-20, \Delta V = +10$ to $+30$ cm^{3}mol^{-1}

In order to account for the apparent diminution of volume evidently occurring during the activation step, it was proposed that a conformational change from the planar to a pyramidal ion was involved [3] . This could also account for the rates of these reactions being exceptionally slow for ionic recombinations.

The conformational change would be accompanied by a concentration of charge onto the central carbon from the highly delocalised cation and could plausibly be accompanied by an increase in solvation . In order to test this hypothesis we have carried out rate measurements on some analogous reactions with diazonium ions, I, in place of the triphenylmethyl cations. It was initially supposed, perhaps naively that such linear species with unhindered electrophilic sites would have no need of conformational changes - indeed none might be available - and so it would be expected that the recombination with an anion would take place with displacement of solvent and a smooth increase in partial molar volume, the transition state being depicted as 1a;

$$\underset{1}{ArN_2^+ + Nu^-} \longrightarrow \underset{1a}{\left[Ar\text{-}N{=}N...Nu \right]^{\ddagger}} \rightarrow \underset{2}{Ar\text{-}N{=}N\text{-}Nu}$$

Reactions of this type have been previously examined and shown to lead to the azo compounds, 2, as sole products, rates being equated with nucleophilicities of the species Nu^- [4]. Benzenediazonium tetrafluoroborates were synthesized according to published procedures and were allowed to react at about 10^{-4}M concentration with nucleophiles at about 10^{-2} M in water or dimethylsulphoxide. The progress of reactions which were carried out in water was followed by the disappearance of the diazonium ion absorbance and was, in all cases, of first order. Rates under these conditions were rather fast and necessitated the use of high pressure stopped flow apparatus [5]. The reaction of p-methoxyphenyldiazonium ion with the nitrobenzoate ion was, by contrast, much slower so that conventional methods could be used. In fact, this reaction was followed by the decrease in conductivity which accompanied product formation. Specific rate constants were used to obtain volumes of activation from eq.1;

$$-RT.d\ \ln k/dp = \Delta V^{\ddagger} \qquad 1$$

Results are given in the Table.

It is evident that volumes of activation for diazonium ion recombinations are quite variable and, from the limited data, it is unwise to set the limits for their values. However, none of the reactions displays the large positive volume of activation which one would expect and all but one show negative values. This seems to rule out either covalent bond formation at the terminal nitrogen or even ion-pair formation as a rate-determining step and once again

Table

Rates of Reaction of Aryldiazonium Ions with Nucleophiles in Water at 25°C (unless otherwise stated).

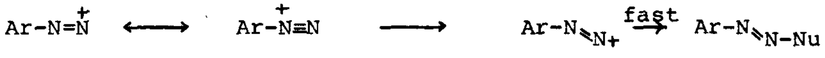
$$p\text{-}XC_6H_4\text{-}N_2^+ + Nu^- \longrightarrow pXC_6H_4\text{-}N{=}N\text{-}Nu$$

a. X=H, $Nu^- = N_3^-$		b. X=H, $Nu^- = HSO_3^-$		c. X=H, Nu = $SO_3^=$	
(NaN_3,0.0506M)		($NaHSO_3$,0.0570M)		(Na_2SO_3,0.0860M)	
p/bar	k/s^{-1}	p/bar	k/s^{-1}	p/bar	k/s^{-1}
45	7.80	40	0.0195	45	0.0279
255	7.60	225	0.0205	250	0.0290
500	7.58	460	0.0220	500	0.0324
750	7.47	710	0.0229	730	0.0344
1000	7.09	970	0.0245	975	0.0392
$\Delta V^{\ddagger}/cm^3mol^{-1}$	+2.2	-9.1		-8.9	± 1

d. X=NO_2,Nu^-= $PhSO_2^-$		e. X=OMe, Nu^- = p-nitrobenzoate	
(Na SO_2Ph = 0.01M)		(tetrabutylammonium p-nitrobenzoate 3.1×10^{-3}M) solvent = DMSO, T=30°	
p/bar	k_{obs}/s^{-1}	p/bar	$10^4k_1/s^{-1}$
10	0.189	1	4.93
250	0.202	300	5.87
500	0.211	600	6.63
750	0.209	900	7.38
1000	0.203		
$\Delta V^{\ddagger}/cm^3$ mol^{-1} =	-1.7 ± 1.1		-15.0 ± 1

require an explanation to be sought in terms of some charge-conserving or charge-concentrating process . Bond formation without charge neutralisation seems rather difficult to accommodate but the results could be consistent with

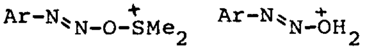
π-complex formation followed by fast rearrangement to the product.
A conformational change as activation step can only be a bond-bending deformation 4 ⟶ 5 which would be expected to bring about a decrease in resonance interaction between the diazonium group and the ring and hence an increase in solvation.



$$\mathrm{Ar{-}N{=}\overset{+}{N}} \longleftrightarrow \mathrm{Ar{-}\overset{+}{N}{\equiv}N} \longrightarrow \mathrm{Ar{-}N{\searrow}N_{+}} \xrightarrow{fast} \mathrm{Ar{-}N{\searrow}N{-}Nu}$$

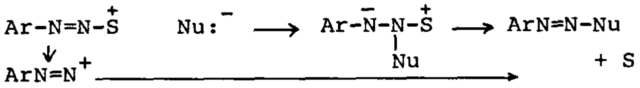
4 5

The volume change for such a process, though plausibly negative should be small as, indeed, are the volumes of activation for the reactions reported above. A third explanation has been considered: the diazonium ions might exist as covalent solvates, 5, 6. There is evidence for such species being present in DMSO. Product formation then could result from rate-determining dissociation to the free diazonium ion or else by an addition-elimination on the solvate analogous to ester hydrolysis. A negative activation volume as is observed appears to be more consistant with the latter mechanism and accords with the more negative value for displacement of the larger ligand (DMSO compared with water) though on present evidence there is little to distinguish these possibilities.



$$\mathrm{Ar{-}N{\searrow}N{-}O{-}\overset{+}{S}Me_2} \qquad \mathrm{Ar{-}N{\searrow}N{-}\overset{+}{O}H_2}$$

5 6



$$\mathrm{Ar{-}N{=}N{-}\overset{+}{S}} \quad \mathrm{Nu{:}^{-}} \longrightarrow \mathrm{Ar{-}\overset{-}{N}{-}\underset{Nu}{N}{-}\overset{+}{S}} \longrightarrow \mathrm{ArN{=}N{-}Nu}$$
$$\mathrm{ArN{=}N^{+}} \longrightarrow \quad + \mathrm{S}$$

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