

ON THE ABSOLUTE REACTIVITY OF ARYL CATIONS:
SELECTIVITY TOWARD HALIDE IONS AS A FUNCTION OF VISCOSITY

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Abstract: The selectivities toward bromide and chloride ions observed in the dediazonation of three arenediazonium salts are found to be independent of viscosity. It is inferred that the capture of aryl cations by these halide ions is diffusion controlled.

Aryl cations are generally considered to be intermediates in the dediazonation of arenediazonium ions in protic solvents at low pH.² These cations have never been directly observed, despite serious efforts,³ and evidence has been presented that they are highly reactive species.⁴ It is likely that they react with nucleophiles at or near the diffusion limit,⁵ k_{diff} c. $10^9 - 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Measurement or estimation of the absolute rate constants of their reactions is a worthy and challenging goal.

Even if aryl cations cannot be observed, one may apply to them a viscosity test of diffusion control:⁶

Since an increase in solution viscosity decreases the rate constant of a diffusion controlled (second or higher order) reaction, the relative rates of two nearly diffusion controlled reactions must decline toward unity with increasing viscosity.

Such behavior has been observed during a study of the trapping of phenyl radicals by I_2 , CBr_4 , $\text{Me}_2\text{CH-I}$, and BrCCl_3 in mixtures of benzene and mineral oil.⁶ In the presence of one I atom donor and one Br atom donor, $k_{\text{I}}/k_{\text{Br}}$ (or its reciprocal) declined from values of 1.6 to 1.1, 2.0 to 1.2, and 6.0 to 2.3. Subsequent studies⁶ showed that the most efficient trap, I_2 , indeed reacted with a rate constant only slightly below the value of k_{diff} calculated for phenyl + I_2 . For ions,⁷ as for molecules and radicals, diffusion rates fall with increasing viscosity.

To test this hypothesis for aryl cations, the mesitylene-, 2,4-xylene-, and (unsubstituted) benzenediazonium ions were subjected to thermal dediazonation at ambient temperature in water, ethylene glycol, and glycerol, in the presence of bromide and chloride ions. The ions were prepared as the fluoborates by the method of Doyle, et. al.,⁸ and purified by the method of Zollinger and coworkers.⁹ The rate of dediazonation of the mesitylene analog in particular is constant in aqueous solution at pH 6 and below.¹⁰ Bromide and chloride ions were selected as nucleophiles because their relative reactivities toward aryl cations are ca. 2.0:1.0,² they should have similar diffusion rates, and they appear inert toward arenediazonium ions themselves. The coefficients of viscosity of water, ethylene glycol, and glycerol at 25° are, resp., 0.9, 13.0, and 954 cP.¹¹ To prevent side reactions, reportedly homolytic, involving the diazotic acid or diazotate, c. 8 vol. % aqueous 0.01 M HBr was added to each solution; the coefficient of viscosity of the resulting glycerol-water solution is estimated to have been c. 400 cP.¹² Dediazonations were conducted for 5 to 10 half-lives (est.) at 21.0-23.5°. Halobenzenes were

DEDIAZONIATIONS IN PROTIC SOLVENTS OF VARIOUS VISCOSITIES

Solvent	Cation	[X ⁻], M.	[ArBr]/[ArCl]		Product Yield, %	
			Hplc column: Cyano-ethyl	C-18	ArBr	ArCl
<u>2,4,6-Trimethylbenzenediazonium (mesitylenediazonium)</u>						
H ₂ O	Na ⁺	0.20	2.03		4.5	2.2
Ethylene Glycol	"	"	2.20		8.8	4.0
H ₂ O	"	0.05	2.07	2.12	1.4	0.65
Ethylene Glycol	"	"	2.13	2.32	4.1	1.8
H ₂ O	Me ₄ N ⁺	0.05	1.91	2.05	1.4	0.7
Ethylene Glycol	"	"	2.10	2.01	3.7	1.7
H ₂ O	Na ⁺	0.055		2.06	1.4	0.66
Methanol	"	"		2.14	5.3	2.5
Glycerol	"	0.057		2.77	4.3	1.5
H ₂ O	"	0.25		2.10	5.7	2.7
Glycerol	"	"		2.33	14.5	6.0
H ₂ O	Li ⁺	0.06		2.12	1.45	0.7
Glycerol	"	"		2.38	4.5	1.9
<u>2,4-Dimethylbenzenediazonium (2,4-xylenediazonium)</u>						
H ₂ O	Na ⁺	0.10		1.73	1.9	1.1
Methanol	"	"		1.86	5.8	3.1
Ethylene Glycol	"	"		1.82	3.8	2.1
Glycerol	"	"		2.15	4.6	2.2
<u>Benzenediazonium</u>						
H ₂ O	Na ⁺	0.10		1.38	1.4	1.0
Methanol	"	"		1.36	3.5	2.6
Ethanol	"	"		1.24	2.9	2.4
Glycerol	"	"		1.78	3.0	1.7

determined by hplc (cyanoethyl or C18 column; aqueous methanol).

The results appear in the table as the ratio $[\text{ArBr}]:[\text{ArCl}]$, which = the selectivity $k_{\text{Br}}/k_{\text{Cl}}$, since $[\text{MBr}] = [\text{MCl}]$ within 1 % in all runs. Absolute (percent) yields are also given. The values of the rate constant ratio in water were as follows:

Mesitylenediazonium,	2.09 ± 0.06 ;
2,4-Xylenediazonium,	1.73;
Benzenediazonium.	1.38 ± 0.03 .

These ratios did not decrease in either ethylene glycol or glycerol. If anything, the ratio in glycerol was slightly greater than in the other solvents. These observations were independent of salt concentration and of the identity of the added cation in a modest number of experiments.

The fact that selectivities are unaffected by viscosity might be explained in two ways:

(1) Absolute rates of aryl cation capture are far below that of diffusion, by as many as three orders of magnitude. Neither rate would then decrease.

(2) Absolute rates for both Br^- and Cl^- are at the diffusion limit. There is no gap between the values of k_{diff} and the operative rate constants. Both rates decrease with increasing viscosity, and to similar extents. The aryl cation reacts with a nearby halide ion, and very likely one with which its precursor, the diazonium ion, has been paired.

The experiments reported here have ruled out for aryl cation capture the intermediate range of absolute rate constants, from c. 10^7 to $10^9 \text{ M}^{-1} \text{ sec}^{-1}$. (The upper limit of this range is the approximate von Smoluchowski rate constant at low viscosity, such as that of water. The lower limit is calculated for a solvent 100 times as viscous, assuming the von Smoluchowski rate constant to be inversely proportional to the first power of the viscosity coefficient.)

A choice between hypotheses (1) and (2) cannot be made on the basis of our data alone.

The second hypothesis is, however, supported by published data. Zollinger and his collaborators⁹ studied the dediazoniations at 25° of benzene- and mesitylenediazonium fluoborates in trifluoroethanol under N_2 , Ar, and mixtures of the gases at 300 atm total pressure. Addition of N_2 up to 300 atm, where $[\text{N}_2] = 3.05 \text{ M}$, decreased the overall rate, while addition of KNCS at 300 atm of either N_2 or Ar increased the rate of dediazoniati o n, and to similar extents. Added N_2 exchanged with N-15 labeled diazonium ion, while rearrangement of the labeled diazonium group—aryl migration from one N atom to the other—occurred to a greater extent, even under 300 atm dinitrogen.

From these and similar experiments the authors inferred that two aryl cation- N_2 molecule pair intermediates, a tight pair and a solvent separated pair, occur during dediazoniati o n. Rearrangement occurs within the tight pair, while capture of aryl cation by solvent and other added nucleophiles involves the solvent separated pair. Capture of aryl cation by added N_2 occurs, as evidenced by both the decrease in dediazoniati o n rate and the exchange of label with added N_2 .

These considerations lead to the following interpretation of the present data:

(1) The occurrence of rearrangement, its persistence under N_2 , and exchange with added N_2 all show that reaction of aryl cation with N_2 is near the range of diffusion control.

(2) The fact that KNCS increases the rate means that thiocyanate traps solvent separated pair,

preventing its return to tight pair and then to diazonium ion.

(3) The fact that KNCS at 0.1 M, with 3.0 M N_2 , has increased the observed dediazonation rate constant above that measured under Ar shows that thiocyanate is as much as 30 times as reactive as N_2 toward aryl cation.

(4) Both (2) and (3) in turn imply that the aryl cation-thiocyanate reaction is also near the range of diffusion control, but these data do not say how close.

(5) Since thiocyanate has been shown to react with aryl cations at about the same rate as bromide,⁴ it follows that the reactions of bromide and chloride with aryl cations are also close to diffusion control.

(6) Finally, our data show that these three reactions are exactly at the diffusion control limit (our second hypothesis). To our knowledge, this is the first convincing demonstration that capture of aryl cations is fully diffusion controlled.

The question remains why k_{Br^-}/k_{Cl^-} is not unity for any of the three aryl cations investigated. One answer is that the diffusion rates of Br^- and Cl^- may not be identical because of different degrees of solvation. Another is that the aryl cation reacts with a member of its solvent cage: when the larger Br^- is one of these, fewer water molecules can be present to compete with it; further, the more ortho-methyl groups present, the more important this factor becomes.

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