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RADICAL NUCLEOPHILIC SUBSTITUTION MECHANISM IN THE REACTIONS OF ARENEDIAZONIUM CATIONS WITH NITRITE ION

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Summary: Reactions of arenediazonium cations with nitrite ion generally believed to involve nucleophilic displacement have been found to occur via single electron transfer where free radicals intervene.

Many reactions formally classified in the earlier literature under the category of nucleophilic displacements have been found in recent years to occur by electron transfer free radical pathways. For example, occurrence of a novel electron transfer mechanism involving free radical intermediates in the reactions of arenediazonium cations with iodide ion was reported from our laboratory.[2,3] This concept has been utilized in rationalizing the overall reactivity in the Sandmeyer type halogenodediazoniations.[4] We now present evidence supporting the occurrence of an electron transfer radical chain nucleophilic substitution mechanism in the reactions of a few arenediazonium cations 1 with nitrite ion.

The reactions of benzenediazonium fluoroborate 1a, p-nitrobenzenediazonium fluoroborate 1b and p-methoxybenzenediazonium fluoroborate 1c, with sodium nitrite in methanol medium, under varying conditions, yielded the products as summarized in the Table. The possibility of aryl cation intermediates in these reactions is ruled out since the reaction with 1b is faster and that with 1c slower compared to that with 1a.[5] The observed sensitivity of these reactions towards photochemical catalysis rules out the possibility of a simple nucleophilic displacement of nitrogen which would also not explain the formation of formaldehyde, dediazoniated products and biaryls in these reactions. Our inability to detect any m-dinitrobenzene or m-nitroanisole among the products in the reactions of 1b and 1c, inspite of careful search, clearly eliminates the possibility of aryne intermediates. The reaction of 1a in presence of acrylonitrile, under nitrogen atmosphere yields polyacrilonitrile, as observed by Beringer and Bodlaender[6] in the reactions of aryliodonium salts with titanous chloride. These arguments coupled with the observed inhibition by oxygen, indicate effective intervention of radicals in these reactions. Indeed, generation of phenyl radicals by the reaction of nitrite ions with benzenediazonium salts in DMSO has been reported[7] to consti-

TABLE: Reactions[a] of arenediazonium fluoroborates 1 with sodium nitrite

Run	Arenediazonium fluoroborate, 1	Molar Ratio $NaNO_2$:1	Atmosphere	% Yield of Products[b]					
				Nitrogen	$R-C_6H_5$	$p-R-C_6H_4NO_2$	$p-R-C_6H_4OH$	Biaryl (Isomers)	CH_2O^c
1	1a	1.00	Nitrogen	100% in 600 sec.	44	13	5	21	35
2	1a	1.00	Oxygen[d]	51% in 1800 sec.	11	4	22	5	10
3[e]	1a	1.00	Nitrogen	100% in 1200 sec.	45	12	5	20	37
4[f]	1a	1.00	Nitrogen	100% in 300 sec.	48	10	3	26	40
5	1b	1.00	Nitrogen	100% in 120 sec.	60	12	4	16	51
6	1b	1.00	Oxygen[d]	80% in 1800 sec.	41	6	21	7	40
7	1b	0.75	Nitrogen	100% in 120 sec.	68	8	2	14	57
8[g]	1c	1.00	Nitrogen	10% in 3600 sec.	8	-	-	-	5

a, 5×10^{-3} mol of $p-R-C_6H_4-N_2^+BF_4^-$ were reacted with $NaNO_2$ in methanol solvent at 0°C.

b, Percentages based on arenediazonium fluoroborates.

c, Estimated as dimedone derivative.

d, Initial oxygen atmosphere was gradually replaced by nitrogen as reaction proceeded.

e, In dark. f, In presence of 5×10^{-5} mol of $CuBr_2$.

g, On addition of diethyl ether, 80% 1c was recovered back.

tute the best preparative method towards homolytic aromatic phenylations. Formation of radicals via conceivable homolysis of covalent diazonitrites,[7] is ruled out since 80% 1c is recovered back in run 8, though the formation of covalent azo compounds in the reactions of 1c with other anions, at 0°C, is a facile process in methanol medium.[8] Furthermore, the time for 100% completion of the reaction of 1b with less than the stoichiometric amount of sodium nitrite (run 7) is same as for the two reactants in equimolar ratio. It is noteworthy in this context that while the nitrite ion, having a redox potential[9] below the threshold value,[4] is oxidized by comparatively weaker oxidizing agents,[10] arenediazonium cations are known to undergo reduction by accepting an electron in the π system.[11]

In view of the foregoing arguments, we propose an electron transfer chain mechanism outlined in the Scheme which accounts for all the observations

SCHEME

$$\underset{\underline{1}}{p\text{-R-}C_6H_4\text{-}\overset{+}{N}{\equiv}N} + NO_2^- \longrightarrow \underset{\underline{2}}{p\text{-R-}C_6H_4\text{-}N{=}\dot{N}} + {}^{\bullet}NO_2 \qquad ..\ (1)$$

$$\underline{2} \longrightarrow \underset{\underline{3}}{p\text{-R-}C_6H_4^{\bullet}} + N_2 \qquad ..\ (2)$$

$$\underline{3} + NO_2^- \longrightarrow \underset{\underline{4}}{[p\text{-R-}C_6H_4\text{-}NO_2]^{\bar{\bullet}}} \qquad ..\ (3)$$

$$\underline{4} + \underline{1} \longrightarrow \underline{2} + p\text{-R-}C_6H_4\text{-}NO_2 \qquad ..\ (4)$$

$$\underline{3} + CH_3OH \longrightarrow R\text{-}C_6H_5 + {}^{\bullet}CH_2OH \qquad ..\ (5)$$

$$\underline{1} + {}^{\bullet}CH_2OH \longrightarrow \underline{2} + {}^{+}CH_2OH \text{ — } CH_2O + H^+ \qquad ..\ (6)$$

$$\underline{3} + R\text{-}C_6H_5 \xrightarrow{-H^{\bullet}} p\text{-R-}C_6H_4\text{-}C_6H_4\text{-R (biaryls)} \qquad ..\ (7)$$

$$2\ p\text{-R-}C_6H_4^{\bullet} \longrightarrow p\text{-R-}C_6H_4\text{-}C_6H_4\text{-R-p} \qquad ..\ (8)$$

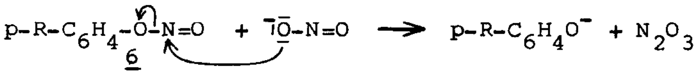
recorded for the title reactions. The diazenyl radical $\underline{2}$ formed by an electron transfer process in step (1), undergoes heterolytic cleavage of the C-N bond to yield gaseous nitrogen and electrophilic π-aryl radical, which reverts to a stable σ-aryl radical[2] $\underline{3}$. This radical may then couple with a nitrite anion to yield a π^* radical anion $\underline{4}$, via a σ^*radical anion,[12] which subsequently transfers an electron to $\underline{1}$ by a $\pi^* \rightarrow \pi^*$ electron transfer process,[11] thus propagating the chain. The chain termination occurs via steps (5), (7) and (8). Owing to high energy requirements of step (3) and good hydrogen atom donating ability of methanol, step (5) is faster than step (3), resulting in lower yields of nitrated products as compared to dediazoniated products. Lower reduction potential[13] of $\underline{1c}$ and slower heterolysis of the C-N bond[2] in $p\text{-MeOC}_6H_4N_2^{\bullet}$ result in retarding the reaction with $\underline{1c}$. The fact that p-methoxyphenyl radical does not couple with nitrite anion,[14] explains the total absence of p-methoxynitrobenzene among the products in run 8. Oxygen inhibits the reaction presumably by scavenging the aryl radicals and interfering with step 4. Steps (3), (5), (6) and (7) are precedented.[15-17]

Phenols, formed in small amounts in these reactions, do not arise due to the presence of oxygen as impurity in nitrogen, since the reaction of $\underline{1a}$ with cuprous bromide using the same batch of nitrogen does not yield any phenol. Also, since aryl cations are not formed, even in small amounts,[18] under our reaction conditions, the possibility of the formation of phenols through these intermediates is ruled out. An alternative, conceivable pathway is the coupling of aryl radicals through the oxygen atom of the ambident nitrite anion, to yield the radical anion 5, though such a coupling of aryl radicals with oxyanions has not been observed in other $S_{RN}1$ reactions.[12] The radical anion 5 could transfer an electron to 1, yielding the nitrite 6.

$$\text{p-R-C}_6\text{H}_4^{\bullet} + {}^{-}\text{O-N=O} \longrightarrow \underset{\underline{5}}{[\text{p-R-C}_6\text{H}_4\text{-O-N=O}]^{\overline{\bullet}}}$$

$$\underline{5} + \underline{1} \longrightarrow \underline{2} + \underset{\underline{6}}{\text{p-R-C}_6\text{H}_4\text{-O-N=O}}$$

Compound 6 may be attacked by a nitrite ion to give a phenoxide anion, which itself or alternatively, the original nitrite 6 may yield phenol on work up.



$$\underset{\underline{6}}{\text{p-R-C}_6\text{H}_4\text{-O-N=O}} + {}^{-}\bar{\text{O}}\text{-N=O} \longrightarrow \text{p-R-C}_6\text{H}_4\text{O}^{-} + \text{N}_2\text{O}_3$$

This mechanism also explains the observed catalysis by cupric bromide in run 4. In aqueous solutions, nitrite ion is known[19] to reduce cupric salts to cuprous salts. The cuprous ion transfers an electron easily to the arenediazonium cation, thereby accelerating the reaction. The fact that catalytic amount of $CuBr_2$ considerably reduces the reaction time, indicates that we are dealing with an oxidation reduction system.

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