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Mechanisms in the Reactions of Arenediazonium Cations with 2-Nitropropanide Anion

Rajive K. Khanna*, Yong M. Jiang

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS-39406, U.S.A.

and

P. R. Singh

Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India

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Abstract: Lithium 2-nitropropan-2-ide reacts, in MeOH solvent, with benzenediazonium and p-methoxybenzenediazonium cations to give diazo-coupled products, but with p-nitrobenzenediazonium cation by competing electron transfer and diazo-coupling reactions.

Free radicals intervene in the reactions of arenediazonium cations with iodide[1] and nitrite[2] ions, but the mode of formation of these intermediates has been debated[3,4] for several years. Single electron transfer from the anion to the highly oxidizing diazonium cation[1,2] and thermal decomposition of the initially formed diazo adduct[5] are suggested alternatives. The reaction of ambident 2-nitropropan-2-ide anion with p-nitrobenzenediazonium cation in Me_2SO solvent has been previously reported[6] to yield p-nitrobenzeneazo-2-(2-nitro)propane. We now present evidence for the occurence of competitive diazo coupling and electron transfer pathways in the reactions of a few arenediazonium cations (1) with 2-nitropropan-2-ide ion, in methanol solvent.

The reactions of benzenediazonium fluoroborate (**1a**), p-methoxybenzenediazonium fluoroborate (**1b**) and p-nitrobenzenediazonium fluoroborate (**1c**) with lithium 2-nitropropan-2-ide in methanol at 0^0 C, afforded the products listed in Table 1. It is noteworthy that the reactions of **1a** and **1b** with 2-nitropropanide anion give the corresponding azo compounds (**2**), namely, benzeneazo-2-(2-nitro)propane and p-methoxybenzeneazo-2-(2-nitro)propane, respectively, in near quantitative yields. Since the high energy (+43 kcal/mol) staggered pyramidalized conformation[7] of 2-nitropropanide anion, with negative charge concentrated on the carbon atom, has a low probability of occurrence, we presume that the formation of azo compounds in these reactions occurs via an electrophilic attack of the beta-nitrogen of the arenediazonium cation on the central carbon of the 2-nitropropanide anion in its more stable planar conformation[7] (reaction 1). Apparently coupling through the oxygen atoms of 2-nitropropan-2-ide does not occur due to high solvation of these electronegative sites by the protic methanol solvent. The azo products from these reactions are stable under our reaction conditions and at room temperature for several days.

$$p\text{-R-}C_6H_4\text{-}N_2^+ + (Me)_2C{=}NO_2^- \longrightarrow p\text{-R-}C_6H_4\text{-N=N-C}(Me)_2NO_2 \qquad (1)$$

Table 1. Reactions[a] of Arenediazonium Fluoroborates **1**, with Lithium 2-Nitropropan-2-ide.

Arenediazonium Floroborate	Reaction Conditions	% Yield of Products[b]						
		N_2	**2**	**3**	**4**	**5**	CH_2O[c]	Biaryls
1a	N_2	-	90[d]	-	-	-	-	-
1a	N_2, 10% Cu(I)[e]	35	54	25	4	-	22	2
1b	N_2	-	85[d]	-	-	-	-	-
1b	N_2, 10% Cu(I)[e]	26	51	20	5	-	17	<1
1c	N_2	40	45[d]	33	3	4	29	2
1c	O_2[f]	16	72	3[g]	-	-	-	-
1c	N_2, 10% Cu(I)[e]	54	35	44	4	5	36	3

[a] Arenediazonium fluoroborate (5 0 mmol) was reacted with equimolar amount of lithium 2-nitropropan-2-ide in degassed MeOH (60 ml) at 0° C until the evolution of N_2 gas ceased (30 min) The reaction mixture was added to 350 ml water and extracted with diethyl ether. [b] Yields are based upon arenediazonium fluoroborate. **2** = $p\text{-}R\text{-}C_6H_4\text{-}N{=}N\text{-}C(Me)_2NO_2$, **3** = $R\text{-}C_6H_5$; **4** = $p\text{-}R\text{-}C_6H_4\text{-}C(Me)_2NO_2$, **5** = $(CMe_2NO_2)_2$ [c] Estimated as dimedone derivative [d] The areneazo-2-(2-nitro)propanes were observed to be stable under our reaction conditions 5 00 mmol of areneazo-2-(2-nitro)propane was stirred in 30 ml deareated MeOH at 0° C for 3 hr On subsequent workup, the starting azo compound was recovered back quatitatively by column chromatography of the reaction mixture Benzeneazo-2-(2-nitro)propane (yellow oil) IR(neat, cm^{-1}) 1550(s), 1380, 1365, 851 p-Methoxybenzeneazo-2-(2-nitro)propane (light yellow solid) mp 94-96° C, IR(KBr pellet, cm^{-1}) 1550(s), 1370, 1360, 1260(s), 840 p-Nitrobenzeneazo-2-(2-nitro)propane (yellow solid) mp 104-106° C, IR(KBr pellet, cm^{-1}) 1545(s), 1390, 1370, 860, 848 [e] 0.5 mmol cuprous bromide [f] Initial oxygen atmosphere was gradually replaced by nitrogen as reaction proceeded

[g] In addition p-nitrophenol (11%) was also formed

In contrast to these reactions of **1a** and **1b**, **1c** reacts with the 2-nitropropanide anion to yield both the azo coupling and the dediazoniated products, with the evolution of nitrogen gas. Since **1c** is stable under our reaction conditions, formation of hydrodediazoniated product (**3**) i.e. nitrobenzene by the thermolysis of p-nitrobenzenediazonium cation may be ruled out. We observe that p-nitrobenzeneazo-2-(2-nitro)propane is also stable under our reaction conditions, which eliminates the possibility of dediazoniation occuring via thermal decomposition of this product Furthermore, we observe that in the presence of oxygen, the yield of p-nitrobenzeneazo-2-(2-nitro)propane increases while dediazoniation is suppressed.

In view of these observations and the known ability of arenediazonium cations to act as good one electron oxidants[8] and that of 2-nitropropanide anion to reduce even comparatively weaker substrates,[9] we propose an electron transfer chain mechanism outlined in the Scheme which accounts for all the observations recorded for the title reactions.

Scheme

$$\underset{\mathbf{1c}}{p\text{-}NO_2\text{-}C_6H_4\text{-}N_2^+} + (Me)_2C{=}NO_2^- \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}N_2^{\cdot} + (Me)_2\dot{C}NO_2 \tag{2}$$

$$p\text{-}NO_2\text{-}C_6H_4\text{-}N_2^{\cdot} \longrightarrow p\text{-}NO_2\text{-}C_6H_4^{\cdot} + N_2 \tag{3}$$

$$p\text{-}NO_2\text{-}C_6H_4^{\cdot} + CH_3\text{-}OH \longrightarrow NO_2\text{-}C_6H_5 + {}^{\cdot}CH_2\text{-}OH \tag{4}$$

$${}^{\cdot}CH_2\text{-}OH + \mathbf{1c} \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}N_2^{\cdot} + {}^{+}CH_2\text{-}OH \tag{5}$$

$${}^{+}CH_2\text{-}OH \longrightarrow CH_2O + H^+ \tag{6}$$

$$p\text{-}NO_2\text{-}C_6H_4^{\cdot} + NO_2\text{-}C_6H_5 \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}C_6H_4\text{-}NO_2 \text{ (biaryls)} \tag{7}$$

The σ-p-nitrodiazenyl radical[10] formed by an electron transfer process in step (2), undergoes heterolytic cleavage of the C-N bond to yield gaseous nitrogen and electrophilic σ-aryl radical. This σ-p-nitrophenyl radical may then abstract a hydrogen atom from MeOH solvent[11] to yield nitrobenzene or attack the initially formed nitrobenzene to yield a mixture of isomeric dinitrobiphenyls.[12] The p-nitrophenyl radical may also couple with the 2-nitropropanide anion to yield small amounts of 2-(p-nitrophenyl)-2-nitropropane by an $S_{RN}1$ mechanism.[13] Owing to the high energy requirements[14,15] of coupling of the electrophilic p-nitrophenyl radical with delocalized nitronate anion and good hydrogen donating ability of MeOH, nitrobenzene is formed in preference to 2-(p-nitrophenyl)-2-nitropropane. The highly reducing[16] hydroxymethyl radical formed in step (4) may then transfer an electron to **1c**, thus propagating the electron transfer chain. Oxygen inhibits the reaction[17,18] presumably by scavenging the p-nitrophenyl and hydroxymethyl radicals. This radical chain mechanism also explains the formation of CH_2O in these reactions. Small amounts of 2,3-dinitro-2,3-dimethylbutane (**5**) may form from the coupling of 2-nitropropyl radicals formed in step (2).

The p-nitrophenyl radical is a good single electron oxidant and may accept an electron from 2-nitropropanide anion yielding p-nitrophenyl anion,[19] which may subsequently produce nitrobenzene on work up or by abstracting a proton from the solvent, thus contributing to chain termination.

$$p\text{-}NO_2\text{-}C_6H_4^{\cdot} + (Me)_2C{=}NO_2^- \longrightarrow p\text{-}NO_2\text{-}C_6H_4^- + (Me)_2\dot{C}NO_2 \tag{8}$$

$$p\text{-}NO_2\text{-}C_6H_4^- \xrightarrow[\text{MeOH}]{\text{H}^+ \text{ from workup or}} NO_2\text{-}C_6H_5 \tag{9}$$

Due to the lower reduction potentials[20] of **1a** and **1b**, 2-nitropropanide anion is unable to reduce them by the transfer of an electron. Consequently only the azo coupling reaction is observed. Indeed, we observe that in the presence of catalytic amounts (10% mol) of highly reducing cuprous bromide,[21] even **1a** and **1b** react with 2-nitropropanide anion to produce N_2 gas. The amount of nitrogen gas evolved with the attendant dediazoniation reaction is much larger than expected from the electron transfer reduction of arenediazonium cations by Cu(I). Thus an induced radical chain mechanism[22] (reaction 10-12) may account for the formation of hydrodediazoniated and other products in these reactions as well.

$$\text{p-R-}C_6H_4\text{-}N_2^+ + \text{Cu(I)} \longrightarrow \text{p-R-}C_6H_4^{\cdot} + N_2 + \text{Cu(II)} \tag{10}$$

$$\text{p-R-}C_6H_4^{\cdot} + CH_3\text{-OH} \longrightarrow \underset{\mathbf{3}}{\text{R-}C_6H_5} + {}^{\cdot}CH_2\text{-OH} \tag{11}$$

$$^{\cdot}CH_2\text{-OH} + \mathbf{1} \longrightarrow \text{p-R-}C_6H_4\text{-}N_2^{\cdot} + CH_2O + H^+ \tag{12}$$

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