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RADICAL MECHANISM OF AROMATIC 'NUCLEOPHILIC' SUBSTITUTION

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Recently, Kim and Bunnett[2] and we[3] simultaneously proposed a new radical mechanism for some reactions which formally appear to be aromatic nucleophilic substitutions. These views find further support from the results of our studies on the uncatalysed reactions of para-substituted benzenediazonium cations with the iodide ion as reported in this communication.

Our observations on the reaction of p-nitrobenzenediazonium fluoborate with potassium iodide under different conditions are summarized in Table I.

Table I : Reaction of p-nitrobenzenediazonium fluoborate with potassium iodide[a]

Molar ratio of KI to $p\text{-}NO_2C_6H_4N_2^+BF_4^-$	Reaction atmosphere	Reaction time	% Yield of the products			
			$p\text{-}NO_2C_6H_4I^e$	$PhNO_2^e$	I_2^c	$CH_2O^{d,e}$
1.00	Nitrogen	100% complete within 60 sec.	45	30	10	36
1.00	Oxygen[b]	Only 80% over in 300 sec.,no appreciable reaction thereafter	28	2	19	2
0.75	Nitrogen	100% complete within 60 sec.	32	35	9	39

[a] $5x10^{-3}$ mole of $p\text{-}NO_2C_6H_4\overset{+}{N_2}\overset{-}{BF_4}$ was reacted with KI in methanol solvent at 0°C; [b] initial oxygen atmosphere was gradually replaced by nitrogen atmosphere as the reaction proceeded; [c] % iodide converted to iodine; [d] estimated as dimedone derivative; [e] percentage based on p-nitrobenzenediazonium fluoborate.

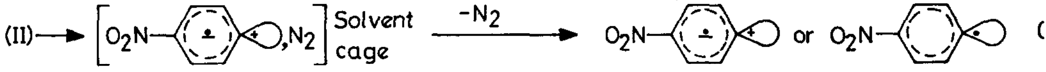
When 5 x 10^{-3} mole of aryldiazonium fluoborate was allowed to react with equimolar amount of potassium iodide in methanol solvent at 0°C under nitrogen atmosphere, the time taken for 100% completion of the reaction as determined by the evolution of theoretical quantity of nitrogen gas was 180 sec. for $C_6H_5N_2^+BF_4^-$, < 60 sec. for $p\text{-}NO_2C_6H_4N_2^+BF_4^-$ and 1200 sec. for $p\text{-}CH_3OC_6H_4N_2^+BF_4^-$. Thus, in comparison with the reference substituent hydrogen, the electron withdrawing p-NO_2 group accelerates the reaction while the resonance electron donating p-OCH_3 substituent acts to slow it down. This rules out the possibility of aryl cation intermediates which would require rate retardation in the cases of both the p-NO_2 and p-OCH_3 substituents[4]. The simple nucleophilic displacement of nitrogen in the reaction of p-nitrobenzenediazonium cation with the iodide ion is ruled out because of the known[5] sensitivity of the reaction to photochemical catalysis. This mechanism would also not explain the formation of nitrobenzene, iodine and formaldehyde as the products. Our failure to detect any m-iodonitrobenzene or m-nitroanisole amongst the products of the reaction of p-$NO_2C_6H_4N_2^+BF_4^-$ with KI and m-iodoanisole or resorcinol dimethyl ether amongst the products of the reaction of p-$CH_3OC_6H_4N_2^+BF_4^-$ with KI inspite of a careful search, clearly eliminates the possibility of occurrence of the elimination-addition mechanism (involving aryne intermediates) in these cases. When the reaction of $C_6H_5N_2^+$ with KI was allowed to proceed in presence of acrylonitrile under nitrogen atmosphere, polyacrylonitrile[6] [i.r. absorption bands at 2230 cm^{-1} (CN), 1450 cm^{-1} (CH, CH_2) and 1050 cm^{-1} (C-C skeletal)]was produced as observed earlier by Beringer and Bodlaender[7] in the reactions of aryliodonium salts with titanous chloride. Obviously, these arguments indicate that aryl radicals[8] may be effective intermediates in these reactions. Any argument for the formation of covalent diazoiodide intermediate which could produce radical species by the homolysis of N-I and C-N bonds, is untenable as the time for 100% completion of the reaction of p-$NO_2C_6H_4N_2^+BF_4^-$ with less than stoichiometric amount of KI is found to be the same as for the two reactants taken in 1:1 molar ratio.

Oxidation of the iodide ion by the aryldiazonium cation via single electron transfer[3] is a distinct possibility. Indeed, the ready formation of aryl iodides from diazonium salt solutions and the iodide ion, in contrast with the general need for a cuprous or other catalysts with other halides[9] has been related to the ease of oxidation of the iodide ions to iodine atoms[10]. A hypothesis as to the character of the radical mechanism which accounts for the experimental observations is presented below :

The initiation step appears to be a photochemically catalyzed single electron transfer[3] from the iodide ion to the p-nitrobenzenediazonium cation with the formation of the radical species (II) (step 1) as also observed in the polarographic one electron reduction of the aryldiazonium

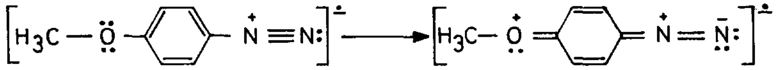
$$\underset{(I)}{p\text{-}NO_2C_6H_4N_2^+} + I^- \longrightarrow \underset{(II)}{[p\text{-}NO_2C_6H_4N_2^+]^{\cdot}} + I\cdot \qquad (1)$$

cations[11]. This radical may undergo a heterolysis of the C-N bond (step 2) to form the electrophilic Π-p-nitrophenyl radical (III) which may transform to σ-p-nitrophenyl radical (IV) (the latter radical is expected to be more stable than the former, e.g. see ref. 12) or the radical (II) may undergo homolytic fission of the C-N bond, directly producing the σ-p-nitrophenyl radical (IV). In view of the polar character of the C-N bond, we prefer the heterolytic cleavage. Apparently, in $[C_6H_5N_2^+]^{\dot{-}}$ and (II), heterolysis of the C-N bond is synchronous with the electron addition to the respective cations and the faster reaction with (I) reflects its greater oxidizing power for the iodide ion. On the other hand, the reaction with $p\text{-}CH_3OC_6H_4N_2^+$ is slower since the heterolysis of the C-N bond in $[p\text{-}CH_3OC_6H_4N_2^+]^{\dot{-}}$ does not take place until after the addition of the electron to the cation as this bond is strengthened due to direct conjugation between the $-N_2^+$ and the $-OCH_3$ groups shown below :

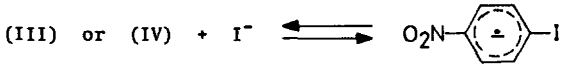


(III) (IV)

(2)



The p-nitrophenyl radical then reversibly combines with the iodide anion according to step 3 (as already known in the literature[13]) to form p-iodonitrobenzene radical-anion (V) which quickly transfers an electron to (I) (step 4) so as to regenerate the p-nitrophenyl radical.



(V)

(3)

$$(V) + (I) \longrightarrow p\text{-}NO_2C_6H_4I + (II) \qquad (4)$$

Formation of nitrobenzene, formaldehyde and iodine may be outlined by means of the following equations :

$$(IV) + CH_3OH \longrightarrow C_6H_5NO_2 + \underset{(VI)}{\cdot CH_2OH} \qquad (5)$$

$$(VI) + (I) \longrightarrow (II) + CH_2\overset{+}{O}H \xrightarrow{-H^+} CH_2O \qquad (6)$$

$$2I\cdot \longrightarrow I_2 \qquad (7)$$

Steps 2,3 and 4 constitute a chain mechanism. Oxygen inhibits the reaction presumably by interfering with this chain process[14] Steps 3,5 and 6 are precedented[13,15,16].

This mechanism also accounts for the polymerization of acrylonitrile and the predicted bimolecularity[4] of these reactions. In addition, it has the potentiality for explaining the observed e.s.r. spectrum[17] of the electrophilic phenyl radical as well as the slow reversibility[18] of the C-N bond heterolysis at the solvent cage stage in step 2.

Further experiments designed to test the validity of this mechanism are in progress and will be reported in detail subsequently.

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NOTES AND REFERENCES

1. Author to whom correspondence should be addressed.
2. J.K. Kim and J.F. Bunnett, J. Amer. Chem. Soc., **92**, 7463, 7464 (1970).
3. P.R.Singh and Ramesh Kumar, Proc. 58th Indian Sci. Cong. Part III (Abstracts), 210 (1971).
4. E.S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, 1959, pp. 457, 458.
5. M.D. Johnson, J. Chem. Soc., 805 (1965).
6. Control experiments without either $C_6H_5N_2^+$ or KI under otherwise identical conditions did not produce any polyacrylonitrile.
7. F.M. Beringer and P. Bodlaender, J. Org. Chem., **34**, 1981 (1969).
8. Formation of p-nitrophenyl cation by the oxidizing action of p-$NO_2C_6H_4N_2^+$ on the p-nitrophenyl radical may be considered, but the absence of any significant amount of the aryl methyl ether amongst the products does not support this view; similarly, formation of the p-nitrophenyl anion by the reducing action of the iodide ion on the p-nitrophenyl radical may be considered, but this anion would not account for the formation of p-iodonitrobenzene and formaldehyde.
9. H.H. Hodgson, S. Birtwell and J. Walker, J. Chem. Soc., 770 (1941).
10. J.G. Carey, G. Jones and I.T. Millar, Chem. Indus., 1018 (1959).
11. R.M. Elofson and F.F. Gadallah, J. Org. Chem., **34**, 854 (1969).
12. P.H. Kasai, P.A. Clark and E.B. Whipple, J. Amer. Chem. Soc., **92**, 2640 (1970).
13. D.E.Bartak, W.C. Danen and M.D. Hawley, J. Org. Chem., **35**, 1206 (1970).
14. N. Kornblum and F.W. Stuchal, J. Amer. Chem. Soc., **92**, 1804 (1970).
15. A.L.J. Beckwith and R.O.C. Norman, J. Chem. Soc. (B), 403 (1969).
16. D.F. DeTar and M.N. Turetzky, J. Amer. Chem. Soc., **77**, 1745 (1955).
17. R.A.Abramovitch and J.G. Saha, Canadian J. Chem., **43**, 3269 (1965).
18. E.S. Lewis and J.M. Insole, J. Amer. Chem. Soc., **86**, 32 (1964).