Competition between Radical and Nonradical Reactions of Halonitrobenzenes in Alkaline Alcoholic Solutions

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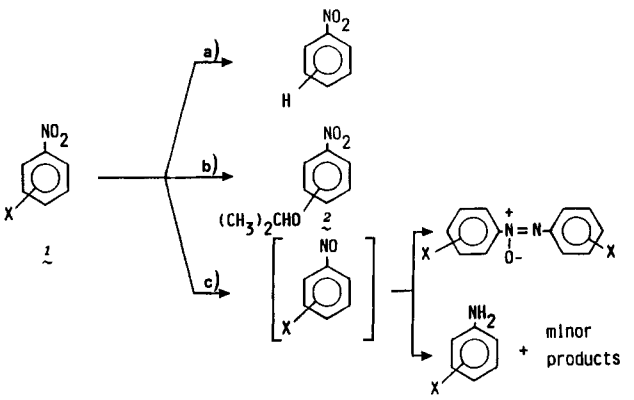
The study of the reactivity of monohalonitrobenzenes in 2-propanol solutions of potassium 2-propoxide has led to the identification of three distinct reaction paths: (a) hydro dehalogenation to nitrobenzene, (b) alkoxy dehalogenation via the S_NAr mechanism, and (c) nitro reduction to azoxy and anilino derivatives via nitroso intermediates. With the exception of 2- and 4-fluoronitrobenzene, radical processes c or a are faster than the S_NAr reaction. The radical processes proceed via a common intermediate, the radical anion $[XC_6H_4NO_2]^{\bullet-}$, which can undergo unimolecular fragmentation to nitroaryl radical and X^- (path a, favored for X = 2-I, 2-Br), or reduction to the dianion $[XC_6H_4NO_2]^{2-}$, the direct precursor of the nitroso intermediate XC_6H_4NO (path c). In the presence of oxygen, an effective oxidant of the radical-anion intermediate, the S_NAr reaction prevails for the activated ortho and para substrates. Cation–anion interactions are also of major consequence in determining the course of reaction. Ion pairing favors nitro reduction, whereas it slows both the S_NAr and the hydro dehalogenation reactions.

One major effect of nitro substitution in organic compounds is the enhancement of their electrophilic reactivity. The interaction of nitroarenes with electron-rich reagents can lead to products of electron transfer, charge transfer, nucleophilic attack on a ring carbon (Meisenheimer complexes), and, in the case of basic anionic nucleophiles, proton transfer.[1,2] Occasionally two or more of these processes take place with comparable rates in a given nitroarene/nucleophilic/solvent system and lead to different final products.

One interesting case is that of 1-chloro-4-nitrobenzene in alkaline 2-propanol solutions. Earlier work has shown that in this system the rate of substrate consumption and the products formed change depending on the presence or absence of oxygen in the reacting solution.[3] In the absence of oxygen, products derived from reduction of the nitro group were obtained, including 4,4′-dichloroazoxybenzene (the main product) and 4-chloroaniline.[3,4] When the reaction was conducted in vessels opened to the atmosphere, nitro reduction was greatly inhibited and the product of alkoxy dehalogenation was obtained along with minor amounts of 4-nitrophenol.[3,5] From these and further studies,[3-8] it was established that nitro reduction proceeds via radical intermediates and is, for 4-chloronitrobenzene, faster than alkoxy dehalogenation via the addition/elimination (S_NAr) mechanism. It was also noted that ion-pairing phenomena have significant kinetic effects on both processes.[5-8]

The diverse reactivity displayed by 1-chloro-4-nitrobenzene prompted us to extend these investigations to the complete series of monohalonitrobenzenes so as to assess the effects on reactivity due to the nature of the halogen substituent, to its orientation relative to the nitro group,

Scheme I



and to the presence in solution of molecular oxygen and of cation complexing agents.

Results

The reactions of 12 halonitrobenzenes $XC_6H_4NO_2$ 1 (X = F, Cl, Br, I) were studied in anhydrous 2-propanol solutions containing a 10-fold excess of potassium 2-propoxide. Each substrate was examined under four standard sets of reaction conditions: i.e., *anaerobic* and *aerobic*, *with* and *without* the K^+ complexing 18-crown-6 ether.

Depending on X and its site of substitution, as well as on the reaction conditions used, any of the products shown in Scheme I can be obtained.

These products arise from three distinct reaction channels: i.e., (a) hydro dehalogenation, (b) alkoxy dehalogenation, and (c) nitro reduction.

Table I summarizes the kinetic and product data for anaerobic reactions run with $(CH_3)_2CHOK$ (left-hand side) and with $(CH_3)_2CHO^-/K^+$–18-crown-6 (right-hand side). Product data are expressed with reference to Scheme I as the percent fraction of each reaction channel and were established as follows. For channels a and b, each leading to a single product, the percent yields are reported of nitrobenzene and of nitrophenyl 2-propyl ether, respectively. The percent fraction of channel c was calculated as the complement to 100% for the sum of the percent of a and b, whenever $XC_6H_4NN(O)C_6H_4X$, the major product of nitro reduction, could be qualitatively identified by GC and GC–MS analysis. This procedure was followed for convenience since quantitation of all of the numerous products of nitro reduction,[4] reaction c, was not practical.

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Table I. Reactivity Data for the Reaction of Halonitrobenzenes $XC_6H_4NO_2$ (1) with $(CH_3)_2CHOK$ in $(CH_3)_2CHOH$ at 75 °C and under Argon, with and without 18-Crown-6[a]

	without 18-crown-6				with 18-crown-6			
		product distribution,[c] %				product distribution,[c] %		
X	10^5k_ψ,[b] s^{-1}	a	b	c	$10^5k_\psi^{crown}$,[d] s^{-1}	a	b	c
2-F	4100	0	99	0	3200	0	92	0
3-F	98	0	0	100	6.0	0	0	100
4-F	300	0	93	0	6900	0	96	0
2-Cl	140	3	13	84	14	19	72	0
3-Cl	160	0	0	100	10	0	0	100
4-Cl	71	0	0	100	64	0	94	0
2-Br	(25 min)	72	3	0	(7 min)	90[e]	2	0
3-Br	150	0	0	100	7.8	1	0	99
4-Br	100	1	1	98	48	4	86	0
2-I	(5 min)	98	0	0	(2 min)	100[e]	0	0
3-I	110	0	0	100	(34 min)	65	0	35
4-I	120	2	0	98	(17 min)	64[e]	9	0

[a] The substrate concentration was 0.02 M; $(CH_3)_2CHOK$ was 0.22–0.23 M. [b] Pseudo-first-order rate constant obtained from the slope of linear plots ln $[XC_6H_4NO_2]$ vs time. The time required for complete substrate consumption is given in parentheses under this heading for reactions that yield nonlinear ln $[XC_6H_4NO_2]$ vs time plots (see text). [c] With reference to Scheme I and determined as described in the text. [d] As in *b*, relative to experiments in which 18-crown-6 was present in 0.29–0.30 M concentration. [e] Data confirmed by potentiometric titration of I^- released.

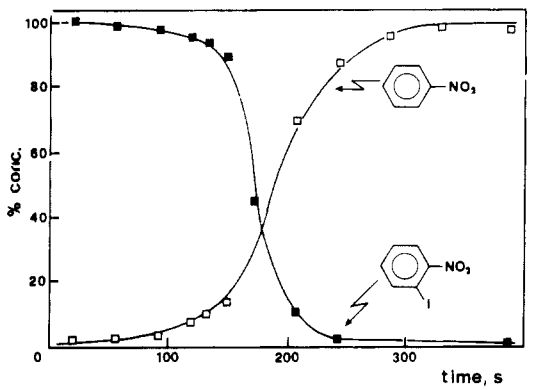

Figure 1. Time dependence of the concentration of reactant and product for the reaction of 2-iodonitrobenzene (0.02 M) with $(CH_3)_2CHOK$ (0.22 M) in $(CH_3)_2CHOH$ at 75 °C under Ar.

Kinetic data are expressed as pseudo-first-order rate constants for those systems that yield linear plots of ln [1] vs time. For those systems that follow more complex kinetic laws and display evident downward curvature in the plot of ln [1] vs time, kinetic data are expressed, very crudely, as the time required for substrate consumption (<1% of the initial concentration). In this study, linear plots were invariably observed for all systems that reacted along paths b, c, or b + c in various proportions. Reactions that produced significant amounts of nitrobenzene, in contrast, gave nonlinear ln [1] vs time plots. An example of a typical concentration vs time curve is shown in Figure 1, which reports the time dependence of substrate and product concentrations for the reaction of 2-iodonitrobenzene, which produces nitrobenzene as the only product (100% a).

The most significant results are summarized in the following points.

Experiments with $(CH_3)_2CHOK$ under Argon. Nitro reduction (path c) is the dominant or exclusive process for all four *m*- and *p*-halonitrobenzenes (with the exception of 4-fluoronitrobenzene). It is also the major path in the reaction of 2-chloronitrobenzene.

2-Fluoro- and 4-fluoronitrobenzene are rapidly and quantitatively converted via path b to the corresponding nitrophenyl 2-propyl ethers, the former proceeding at a faster rate. Minor components of alkoxy dehalogenation are also observed in the reactions of 2-chloro- (13%) and 2-bromonitrobenzene (3%).

Hydro dehalogenation (path a) is the exclusive path followed by 2-iodonitrobenzene and the major (72%) component in the reaction of 2-bromonitrobenzene. It also occurs, to a minor extent, with 2-chloro- (3%) and 4-iodonitrobenzene (2%).

Experiments with $(CH_3)_2CHO^-/K^+$–18-Crown-6 under Argon. The addition of 18-crown-6 produces only a variation in the rate of reaction for some substrates; for others it also brings about a variation in the product distribution. From the former cases, the sign and magnitude of the kinetic effect due to ion pairing can be assessed for each individual reaction shown in Scheme I. Specifically, when cation K^+ is complexed by 18-crown-6, the following are found: Nitro reduction proceeds at a reduced rate as evident from the data for 3-fluoro- (k_ψ/k_ψ^{crown} = 16), 3-chloro- (k_ψ/k_ψ^{crown} = 16), and 3-bromonitrobenzene (k_ψ/k_ψ^{crown} = 19). Hydro dehalogenation proceeds at increased rate, as indicated qualitatively by the data for 2-iodo- and 2-bromonitrobenzene. Alkoxy dehalogenation also proceeds at increased rate: k_ψ^{crown}/k_ψ is 23 for 4-fluoronitrobenzene (the opposite kinetic effect is, however, observed with 2-fluoronitrobenzene; k_ψ/k_ψ^{crown} = 1.3).

Thus, ion pairing favors nitro reduction (path c) and inhibits hydro dehalogenation (path a) and alkoxy dehalogenation (path b).

As a result of the effects described above, suitable substrates give different products depending on the presence or absence of 18-crown-6. This is the case with 4-chloronitrobenzene, which, upon addition of 1.3 equiv of 18-crown-6 to the potassium alkoxide solution, gives the product of alkoxy dehalogenation in quantitative yield. Interestingly, the substrate reacts with similar rates (k_ψ = 7.1×10^{-4} s^{-1} and k_ψ^{crown} = 6.4×10^{-4} s^{-1}) under the two sets of conditions, with and without 18-crown-6, leading, however, to different products. Indeed we find that the balance between nitro reduction and alkoxy dehalogenation for this substrate can be finely tuned by varying the ratio [18-crown-6]/[$(CH_3)_2CHOK$], i.e., the extent of cation complexation, as shown in Figure 2. The plot shows the results, on the basis of product and kinetic analysis, of five experiments in the form of the pseudo-first-order rate constants for alkoxy dehalogenation, k_ψ^b, and nitro reduction, k_ψ^c. These were evaluated from k_ψ, the observed pseudo-first-order rate constant for substrate consumption, as follows. The value of k_ψ^b was calculated from the slope of $\{[4\text{-}(CH_3)_2CHOC_6H_4NO_2]/[4\text{-}ClC_6H_4NO_2]\}_t$ vs $1 - e^{-k_\psi t}$

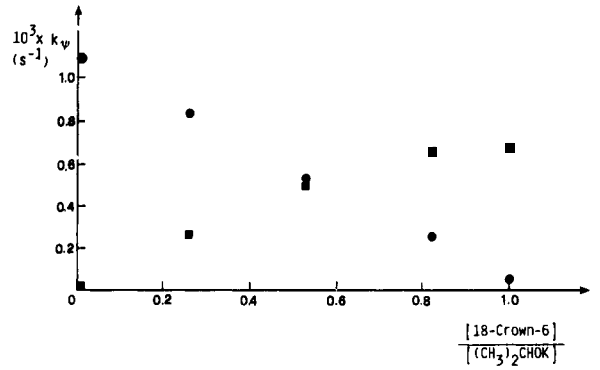

Figure 2. Effect of 18-crown-6 on the reactivity of 4-chloronitrobenzene (0.02 M) with $(CH_3)_2CHOK$ (0.265 M) in $(CH_3)_2CHOH$ at 75 °C under Ar. Circles (●) and squares (■) refer to the rates of nitro reduction, k_ψ^c, and alkoxy dehalogenation, k_ψ^b, respectively. These were evaluated from the observed pseudo-first-order rate constant and the product distribution, as detailed in the text.

plots, while k_ψ^c was estimated as the difference $k_\psi - k_\psi^b$.

As is the case with 4-chloronitrobenzene, the reactivity of 4-bromonitrobenzene changes from nitro reduction to alkoxy dehalogenation when K^+ is complexed by 18-crown-6. In addition, a minor component (4%) of hydro dehalogenation is also observed. Nitro reduction becomes less prominent and is absent in solutions of 18-crown-6-complexed K^+ with 3- and 4-iodonitrobenzene, respectively. For these substrates, however, hydro and not alkoxy dehalogenation is the process that becomes competitive and prevails.

Experiments with $(CH_3)_2CHOK$ and with $(CH_3)_2CHO^-/K^+$–18-Crown-6 under Air. All the experiments of Table I were repeated in reaction vessels opened to the atmosphere and led to the following observations. The four 3-halonitrobenzenes display, under these conditions, both with and without 18-crown-6, an almost insignificant reactivity. After a few days at 75 °C, these substrates were still largely unreacted, and only traces of the main products of nitro reduction (azoxy and anilino derivatives) were detected by GC analysis.

2-Fluoro- and 4-fluoronitrobenzene give the substitution products, path b, in quantitative yields (>92%) at rates that are equal, within experimental error, to those measured under anaerobic conditions both with and without 18-crown-6.

The reactions of the 4-chloro-, 4-bromo-, and 4-iodonitrobenzene with $(CH_3)_2CHOK$ give quite different results when O_2 is present in the solutions. The rates of substrate consumption are considerably smaller ($k_\psi = 1.2 \times 10^{-5}$, 1.2×10^{-5}, and 0.7×10^{-5} s^{-1} for the 4-chloro, 4-bromo, and 4-iodo derivative, respectively), and the products of nitro reduction are not formed. The substitution product, **2**, forms in poor to moderate yields and is accompanied by minor amounts of 4-nitrophenol. In the presence of $(CH_3)_2CHO^-/K^+$–18-crown-6, 4-chloronitrobenzene reacts similarly ($k_\psi = 55 \times 10^{-5}$ s^{-1}, 95% of **2**) as it does under an argon atmosphere. 4-Bromonitrobenzene behaves similarly except for the absence of nitrobenzene, formed in 4% yield in the anaerobic experiment. In the case of the 4-iodo derivative a more drastic change was observed since no nitrobenzene formed (64% in the anaerobic reaction) and the substitution product **2** was obtained in 77% yield, with a pseudo-first-order rate constant for substrate consumption of 28×10^{-5} s^{-1}.

In the presence of oxygen, the reactions of 2-chloro-, 2-bromo-, and 2-iodonitrobenzene with $(CH_3)_2CHOK$ also proceed at lower rates and give product distributions different from those carried out anaerobically. The substitution product **2** is the only product in the reactions of 2-chloro- and 2-bromonitrobenzene (98% yield in each case; $k_\psi = 8.1 \times 10^{-5}$ and 4.6×10^{-5} s^{-1}, respectively), whereas the 2-iodo derivative gives two products, nitrobenzene (24%) and ether **2** (50%).

In the reactions with $(CH_3)_2CHO^-/K^+$–18-crown-6, the 2-chloro derivative reacts exclusively along path b ($k_\psi = 8.8 \times 10^{-5}$ s^{-1}) and the 2-bromo derivative is consumed in 420 min (vs 7 min in the anaerobic experiment) to give nitrobenzene (47%) and the ether **2** (25%), whereas 2-iodonitrobenzene gives primarily nitrobenzene (97%) and a minor amount (2%) of **2** in 26 min (vs 2 min in the anaerobic experiment).

The effect of oxygen on the processes of Scheme I can thus be summarized as follows: Path a, hydro dehalogenation, is inhibited by O_2, although not suppressed, as shown by the reactivity of 2-iodonitrobenzene. Path b, alkoxy dehalogenation, is not affected by O_2, as shown by the reactivity of 2-fluoro- and 4-fluoronitrobenzene. Path c, nitro reduction, is quite efficiently inhibited by O_2, as shown by the lack of reactivity of the *m*-halonitrobenzenes, even after prolonged treatment at 75 °C.

Discussion

The results reported in this paper reveal that the reaction of monohalonitrobenzenes in alkaline 2-propanol solutions can take three distinct pathways, each leading to specific products (Scheme I). A first clear-cut distinction is made on the basis of the effect of oxygen, a known oxidant of nitroaryl radical anions.[9] Hydro dehalogenation (a) and nitro reduction (c) are strongly inhibited; alkoxy dehalogenation (b) is unaffected by oxygen. Substantiated by additional evidence that is discussed later, these effects indicate that competition operates in these systems among two radical (a and c) and one nonradical (b) path.

All of the features observed in this study for the alkoxy dehalogenation process b are consistent with the S_NAr mechanism of nucleophilic aromatic substitution. The reaction rate is first-order in substrate and in nucleophile, it is insensitive to the presence of O_2, and it displays the characteristic leaving group ($F \gg Cl \simeq Br \simeq I$) and positional (ortho > para ≫ meta) reactivity orders. Our value of k^{ortho}/k^{para} of 14 for the fluoronitrobenzenes at 75 °C is roughly in the same range of the value (20.4) reported for the same reaction at 25 °C.[10] The kinetic effects observed upon addition of 18-crown-6 also have precedent in the literature. Increased reaction rates have been explained as due to an enhancement of the alkoxide nucleophilicity owing to removal of the tightly bound and shielding counterion K^+.[5-6,11] 2-Fluoronitrobenzene, in contrast, displays a reduced reactivity in the presence of 18-crown-6-complexed K^+. Similar observations were reported for the reaction of 2-fluoronitrobenzene with *t*-BuOK in *t*-BuOH.[11] It was suggested that, in the reaction with ion-paired *tert*-butoxide, bridging of the potassium cation between the alkoxide oxygen and the nitro group oxygens provides specific stabilization of the transition state for nucleophilic attack at the carbon bearing the fluorine substituent. When K^+ is complexed by 18-crown-6 ether, this specific solvation of the transition state is lost and the rate of reaction is reduced.[11] An analogous ex-

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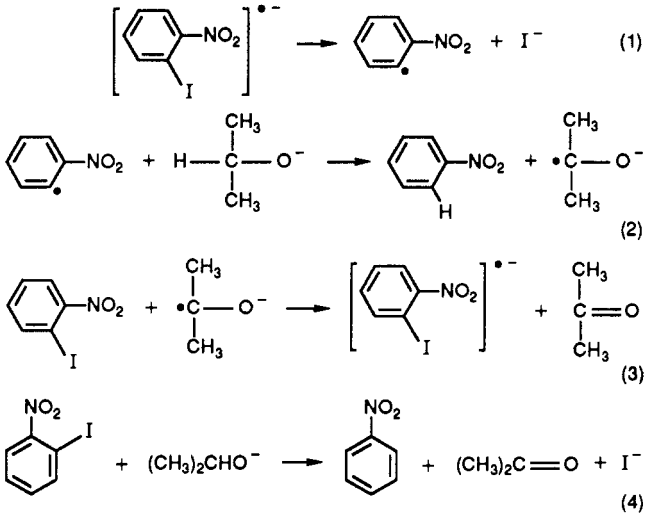
planation probably applies to our data.

The two radical processes (a and c) have distinct kinetic behavior. The shape of the [substrate] vs time plot of reaction a (Figure 1) is typical of a chain process. Inhibition by oxygen, the leaving group reactivity order (I > Br), and the high reactivity of the ortho isomers provide evidence for a radical-chain mechanism of the type described in the literature for the reductive dehalogenation of aryl halides in alkaline alcoholic solutions induced by a radical initiator[12] or, more recently, by electrochemical means.[13] According to this mechanism, the propagation sequence for the reaction of 2-iodonitrobenzene is described by eqs 1–3, the sum of which (eq 4) represents the overall reaction.



In this mechanism, the nitroarene radical anion that is originally formed in some initiation step constitutes the chain propagator. The occurrence of nitroarene radical anions in alkaline alcoholic solutions is amply documented.[8,14] The first step in the propagation sequence involves the fragmentation of the C–halogen bond of the radical-anion intermediate, a process that has been described in the literature as involving the σ^* molecular orbital (MO).[15] An analogous process constitutes one of the propagating steps in the $S_{RN}1$ mechanism of nucleophilic aromatic substitution in haloarenes.[16] The ease of fragmentation, I > Br > Cl, is related to the strength of the C–halogen bond, C–I < C–Br < C–Cl. The presence of a nitro ring substituent greatly reduces the rate of fragmentation of haloarene radical anions[17] because of the enhanced stabilization of the π^* relative to the σ^* MO induced by the nitro substituent. Thus, nitro-substituted aryl halides are unreactive under typical $S_{RN}1$ conditions.[16] It is known, however, from electrochemical measurements in polar aprotic solvents[18–20] that the rate of fragmentation of 2-iodonitrobenzene ($k = 8 \times 10^4$ s^{-1} in DMF) is 5 orders of magnitude greater than that of its meta and para isomers.[19] An analogous trend was observed with the bromonitrobenzenes.[19] The high reactivity of the ortho derivatives was attributed to steric effects, which force the nitro group out of the aromatic ring plane with consequent reduction of the stabilization of the π^* relative to the σ^* orbital. In accord with the electrochemical observations, 2-iodonitrobenzene, the one exception among nitro-substituted aryl halides, was found to undergo $S_{RN}1$ substitution with the enolate of pinacolone.[21]

Our observation, that in the presence of 18-crown-6-complexed K^+ path a proceeds at increased rate, can also be explained in terms of the mechanism described above. Conceivably, a stabilizing effect on π^* results from the interaction of K^+ with the oxygens of the nitro group. Complexation of K^+ by 18-crown-6 removes this extra π^*-orbital stabilization and facilitates the electron transfer from π^* to σ^*. We note that an analogous effect was reported recently, although no explanation was offered.[22] It was observed that, in THF solution, the radical anion of 1,4,6-tri-*tert*-butylnitrobenzene undergoes fragmentation to NO_2^- and aryl radical when 18-crown-6-complexed K^+ was employed, but it is stable in the absence of the crown ether.[22]

Nitro reduction (c) is a multistep process that proceeds via the nitroso derivative as schematically outlined in eq 5.

$$ArNO_2 \xrightarrow[\text{slow}]{+2e^-} ArNO \xrightarrow{+1e^-} \tfrac{1}{2}ArN^+(O^-)=NAr \quad (5)$$

The nitro → nitroso reduction is the slow stage of the overall process and was suggested to take place as shown in eq 6.[7,8] Nitro reduction is quite effectively quenched

$$ArNO_2 \xrightarrow{+1e^-} ArNO_2^{\bullet -} \xrightarrow[\text{slow}]{+1e^-} ArNO_2^{2-} \xrightarrow[-OH^-]{+ROH} ArNO \quad (6)$$

by oxygen.[3,8] Thus, only trace amounts of products of nitro reduction were found at long reaction times when the experiments were carried out without degassing of the solutions. However, when oxygen was excluded from the reaction environment, nitro reduction was the favored reaction path for all monohalonitrobenzenes except 2-iodo- and 2-bromonitrobenzene, which reacted according to path a, and 2-fluoro- and 4-fluoronitrobenzene, which gave the S_NAr reaction (path b). As for the substituent effect on the rate of nitro reduction, the data in Table I for the *m*-halonitrobenzenes indicate that F, Cl, Br, and I behave similarly. An analogous conclusion is reached for the para isomers, 4-$XC_6H_4NO_2$ (X = Cl, Br). From the data of the chloro and bromo derivatives it appears that the meta isomers react at a rate that is ca. 1.5 times that of the corresponding para isomers. In contrast to what is observed for the S_NAr and hydro dehalogenation reactions, ion-pairing facilitates nitro reduction, as indicated in Figure 2. Both inhibition by oxygen and rate depression upon addition of K^+-complexing agents confirm and extend earlier observations.[8]

Conclusions

With the exception of 2-fluoro- and 4-fluoronitrobenzene, the halonitrobenzenes in degassed alkaline 2-propanol solutions undergo reduction via radical processes rather than nucleophilic aromatic substitution. Reduction proceeds via the substrate radical anion and leads, depending on the nature and site of substitution of the halogen, to nitrobenzene, via cleavage of the carbon–halogen bond, or to the highly reactive halonitrosobenzene

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via further reduction of the radical anion.

Work is in progress to achieve a more detailed description of the mechanisms by which the nitroarene radical anion is produced and reduced to a dianion species in these systems.

Experimental Section

GC analyses were performed on a Varian 3700 gas chromatograph interfaced to a Varian 401 CDS Vista Series integrator. A Hewlett-Packard 5890 GC-5970 MSD System was used for GC–MS analysis. ^1H NMR spectra were recorded on a 200-MHz Bruker spectrometer.

Materials. All halonitrobenzenes were commercial samples (EGA Chemie, Carlo Erba, Merck) purified by recrystallization from EtOH or, for the fluoro derivatives, by distillation under reduced pressure. 2-Iodonitrobenzene (EGA Chemie) was best purified by chromatography followed by recrystallization. The purified product was stored in the dark. The cyclic 18-crown-6 ether was prepared and crystallized as the acetonitrile complex, according to the published procedure.[23] Linear-chain hydrocarbons used as internal standards in GC analysis were the GC standards of Carlo Erba. Reagent grade 2-propanol was fractionally distilled from Mg turnings. Solutions of potassium 2-propoxide were prepared by dissolving in 2-propanol under argon a weighed piece of potassium metal, cleaned of oxidized surfaces. The concentration of $(CH_3)_2CHOK$ was determined by titration with standardized HCl solutions. Solutions of $(CH_3)_2CHO^-/K^+$–18-crown-6 were prepared immediately before use by addition of the 2-PrOK/2-PrOH solution to the crown compound, after removal of the acetonitrile by prolonged evacuation of the crown/CH_3CN complex at 40–45 °C.

Kinetic Runs. Anaerobic experiments were performed in a reaction vessel consisting of two arms, connected at their tops by a side arm, each with an independent outlet. A 10- or 20-mL aliquot from a 2-propanol solution of 1 (0.04 M), also containing a suitable C_nH_{2n+2} internal standard for GC analysis, was delivered into one arm, and an equal volume of 0.44 M $(CH_3)_2CHOK$ (or $(CH_3)_2CHO^-/K^+$–18-crown-6) 2-propanol solution was added into the second arm. The reactor was connected to a vacuum/argon line and, after three freeze–thaw cycles, was transferred into a temperature bath kept at 75 °C. After equilibration the two solutions were mixed (time 0). Approximately 1-mL aliquots were withdrawn at desired times by allowing the argon pressure to push the solution into a built-in delivery tube opened to the atmosphere via a three-way air-tight stopcock. Each aliquot, delivered into a test tube containing a chunk of solid CO_2 used to quench the reaction, was diluted with Et_2O and analyzed by GC. For solutions containing 18-crown-6 ether, the crown compound was removed prior to GC analysis by two successive extractions with a nearly saturated KCl aqueous solution. Reactions were followed until substrate concentration was within a few percent of its initial value. Release of I^- and Br^- by substrates undergoing hydrodehalogenation was confirmed and quantified by potentiometric titrations with $AgNO_3$.

Analogous procedures were used for aerobic experiments, which were run in a two-neck flask equipped with a reflux condenser open to the atmosphere.

Product Studies. Product studies were carried out under the same conditions used for kinetic experiments. Reaction products, obtained from the crude organic extracts by low-pressure column chromatography (stationary phase, Kieselgel 60; o.d., 0.015–0.040 mm from Merck; eluant, petroleum ether/toluene mixtures), gave analytical and spectral data in good agreement with literature values and with the structural assignment: 1-(1-methylethoxy)-4-nitrobenzene,[5] 1-(1-methylethoxy)-2-nitrobenzene,[24] 3,3′-difluoroazoxybenzene,[25] and 2,2′-dichloro-,[26] 3,3′-dichloro-,[27] 4,4′-dichloro-,[27] 3,3′-dibromo-,[28] 4,4′-dibromo-,[28] 3,3′-diiodo-,[29] and 4,4′-diiodoazoxybenzene.[30]

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