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Effects of Electron Acceptors and Radical Scavengers on Nonchain Radical Nucleophilic Substitution Reactions

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The yields of reaction products from thermal nucleophilic substitution reactions in dimethyl sulfoxide (DMSO) of six *o*- and *p*-nitrohalobenzenes (**1**) with the sodium salt of ethyl α-cyanoacetate carbanion [$Na^{+-}CH(CN)CO_2Et$) (**2**) were found to be markedly diminished by addition of small amounts of strong electron acceptors (*p*-dinitrobenzene, *m*-dinitrobenzene, and *o*-dinitrobenzene) (Table II), but little or no diminished effects on the yields of reaction products were observed by addition of radical scavengers (such as galvinoxyl, nitroxyl, etc.) (Table III). The results are consistent with the conclusion that these reactions proceed via a nonchain radical nucleophilic substitution mechanism.

Introduction

Over the past three decades, great progress has been made in the field of radical nucleophilic substitution reactions.[1-5] Many reactions long thought to be polar nucleophilic substitution reactions were reinvestigated and found, at least to a certain extent, to proceed via single-electron transfer (SET) reaction mechanisms.[1,2,5-8]

Nucleophilic substitution reactions initiated by photoradiation, solvated electrons, or at electrodes are generally believed to proceed via the chain radical ($S_{RN}1$) mechanism.[2,4,5] Thermal radical nucleophilic substitution reactions have been discovered, however, that are believed to occur by a S_N2-type SET mechanism[6] or a nonchain radical mechanism.[9,10] The first step in the S_N2-type SET or nonchain radical mechanisms is the formation of electron donor–acceptor (EDA) complex followed by a SET reaction to form a radical anion and radical cation pair.[1a] The reactions directed to the final products will then be completed within a solvent cage.[6,9,10] These reactions do not require the initiation by photoradiation, solvated electrons, or an electrode, but obey the second-order kinetics and form the typical S_N2-type rather than the chain-type products.[6,9,10]

In a study of the reactions of *o*-nitrochlorobenzene (**1a**), *o*-nitrobromobenzene (**1b**), *p*-nitrochlorobenzene (**1d**), *p*-nitrobromobenzene (**1e**), and *p*-nitroiodobenzene (**1f**) with the sodium salt of ethyl α-cyanoacetate carbanion [$Na^{+-}CH(CN)CO_2Et$] (**2**) in DMSO, we[10,12] have detected (i) the ESR spectra of the *o*-nitrochlorobenzene radical anion (**3a**), *o*-nitrobromobenzene radical anion (**3b**), *p*-nitrochlorobenzene radical anion (**3d**), *p*-nitrobromobenzene radical anion (**3e**), and *p*-nitroiodobenzene radical anion (**3f**), (ii) the UV spectra of the corresponding EDA complexes, and (iii) the broadening effects of the NMR absorption peaks for the substrates. The kinetics for the formation and decay of the radical anion intermediates **3a**, **3d**, and **3e** in the reactions of **1a**, **1d**, and **1e** with **2**, respectively, determined by means of the ESR F/F lock technique[13] were analyzed by using the e^{-1} mathematical criterion[14a] and computer simulation.[14b] The results were shown to be in good agreement with the successive pseudo-first-order reaction but are not consistent with the chain radical mechanism.[10,12] Based on these results, we have proposed that the thermal reactions of *o*- and *p*-nitrohalobenzenes (**1**) with **2** in DMSO proceed via a nonchain radical nucleophilic substitution mechanism as outlined in Scheme I.

In the present paper, we report the quantitative results of the effects of strong electron acceptors (*o*-dinitrobenzene, *m*-dinitrobenzene, and *p*-dinitrobenzene) and radical scavengers (galvinoxyl, 2-methyl-2-nitrosopropane dimer [$(t\text{-Bu-N=O})_2$], phenyl *tert*-butyl nitrone, 4-ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl, and hydroquinone) on the yields of products from the reactions of **1a**, **1b**, *p*-nitrofluorobenzene (**1c**), **1d**, **1e**, and **1f** with **2**, respectively, in DMSO at 90 °C.

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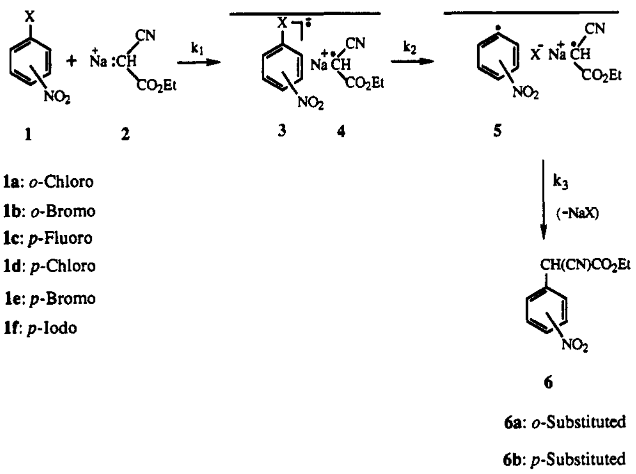
Scheme I



Results and Discussion

Redox Potentials of *o*- and *p*-Nitrohalobenzenes and Dinitrobenzenes. Strong electron acceptors can prevent SET reactions by destroying the radical anion intermediates. *p*-Dinitrobenzene (PDNB), *m*-dinitrobenzene (MDNB), and *o*-dinitrobenzene (ODNB) are very strong electron acceptors and have been widely used as radical anion inhibitors to test for SET reactions.[2a,2d,15] Obviously, the inhibition effects of electron acceptors on the tested SET reactions are highly dependent upon the redox potentials of the radical anion intermediates and the electron acceptors.

The redox potentials of 1, PDNB, MDNB, and ODNB were determined in DMSO solution by cyclic voltammetry. The results are summarized in Table I. Examination of Table I shows that the reduction potentials of PDNB, MDNB, and ODNB are all less negative than the oxidation potentials of the radical anions (**3**) derived from **1** by addition of one electron, indicating that the electron acceptors (PDNB, MDNB, and ODNB) will spontaneously react with the radical anion intermediates **3**. As a result, these electron acceptors can depress the SET reactions of **1** with **2** in DMSO by destroying the radical anion intermediates.

It is interesting to note that the reduction potentials of **1a**, **1b**, **1c**, **1d**, **1e**, and **1f** are in the range of −1.01 ± 0.05 V regardless of the haloatom substituents on the aromatic ring, indicating that the odd electron was directly added to the π^* orbital of the nitro group.[16] The strong electron-withdrawing nitro group will interfere with the intramolecular electron transfer to the σ^* orbital of the C–X bond, which is required for the fragmentation of the C–X bond in the radical anion.[2b] These also explain why the dissociation reactions of phenyl halide radical anions are diffusion-controlled,[4b] but some of the nitrohalobenzene radical anions can stay for a couple of days at room temperature.[10]

Effects of Dinitrobenzenes on the Reactions of *o*- and *p*-Nitrohalobenzenes with the Sodium Salt of Ethyl α-Cyanoacetate Carbanion. In order to ascertain the effects of the electron acceptors and radical scavengers on the reactions of **1** with **2** in DMSO, we set the initial concentration ratios of **2** to **1** at ca. 7. The reactions were quenched before completion for quantitative analysis of the product yields since the reactions of **1** with **2** in DMSO at 90 °C are clean and quantitative.[10,12] The effects of the electron acceptors on the reactions of **1** with **2** are summarized in Table II.

Examination of Table II shows that the yields of the substitution products from the reactions of **1** with **2** were all dramatically decreased by addition of small amounts of PDNB and ODNB, indicating that radical anion species were formed as the reactive intermediates in all of these reactions. These results are consistent with the SET reaction mechanism we have proposed in the previous papers.[10] The inhibition of the product formation resulting from addition of strong electron acceptors is consistent with either a chain (the $S_{RN}1$ mechanism as shown in Scheme II)[2] or nonchain radical mechanism (Scheme I) because radical anions are the reactive intermediates in both radical mechanisms. (We note that the inhibition by strong electron acceptors is one of the criteria suggested for the assignment of the $S_{RN}1$ reaction mechanism.[17]) The Brønsted β_{Nu} values for the nucleophilic substitution reactions of *p*-nitrohalobenzenes with different nucleophiles in DMSO have been found in the range 0.2–0.7, distinctly larger than those for S_N2-type reactions (β_{Nu} = 0.2–0.5),[6c] but not so large as to indicate that these reactions proceed via a SET mechanism (β_{Nu} = 1).[6d] The nucleophilic substitution of *p*-nitrochlorobenzene with PhS^- has been found to proceed via a SET mechanism, however.[11]

In all of the six groups of experiments (Table II), the retardation effects of MDNB are much less efficient than those of PDNB and ODNB. For example, no appreciable diminished effect was observed on the yield of the product from the reaction of **1d** with **2**. The smaller retardation effects of MDNB than those of PDNB and ODNB are certainly associated with its weak electron affinity since the reduction potential of MDNB is ca. 0.30 and 0.1 V more negative than those of PDNB and ODNB, respectively (Table I).

It should be noted that the reaction of **1c** with **2** (entries 9–12 in Table II) was completely prevented by addition of a small amount of PDNB and was almost completely prevented by addition of small amounts of MDNB or ODNB. These results provide conclusive evidence that the reaction of **1c** with **2** in DMSO proceeds via a SET mechanism, albeit the ESR spectrum for the *p*-nitrofluorobenzene radical anion intermediate (**3c**) and the broadening effects of the NMR absorption peaks of the substrate **1c** were failed to be detected,[10,12] and the UV absorption peak of the EDA complex was not distinct.[12] The failure to detect **3c** by spectroscopic methods can be attributed to fast decomposition and thus a low concentration of **3c**.

The *p*-nitrofluorobenzene radical anion is one of the most stable nitrohalobenzene radical anions known due to the strong C–F bond strength and the poor leaving ability of the F^- ion.[18] For example, the dehalogenation rate constants for **3c**, **3d**, **3e**, and **3f** have been determined to be 3×10^{-3}, 6×10^{-3}, 12×10^{-3}, and 0.64 s^{-1}, respectively.[18a] But the reaction yields (Table II) and the failure of the spectroscopic detection of **3c** during the reaction of **1c** with **2** clearly demonstrated that **3c** was much more

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Table I. Redox Potentials of Dinitrobenzenes and *o*- and *p*-Nitrohalobenzenes (1)[a]

	PDNB[e]	MDNB	ODNB[e]	1a	1b	1c	1d	1e	1f
E_{re} (V)[b]	−0.56	−0.85	−0.75	−1.05	−1.10	−1.13	−1.02	−1.01	−1.00
E_{ox} (V)[c]		−0.75		−0.97	−0.95	−0.98	−0.94	−0.92	−0.92
$E_{1/2}$[d]		−0.80		−1.01	−1.03	−1.06	−0.98	−0.97	−0.96

[a] Reversible redox potentials measured in DMSO solution by cyclic voltammetry and referenced to a saturated calomel electrode (SCE), unless otherwise indicated. [b] Reduction potentials of the neutral substrates. [c] Oxidation potentials of the corresponding radical anions derived by addition of one electron. [d] $E_{1/2} = (E_{re} + E_{ox})/2$. [e] Irreversible reduction potentials.

Table II. Effects of Electron Acceptors on the Reactions of *o*- and *p*-Nitrohalobenzenes (1) with $Na^+{}^-CH(CN)CO_2Et$ (2) in DMSO[a]

no.	substrate	$[2]_0/[1]_0$	inhibitor (molar ratio)[b]	time (h)	yield[c] (%) 6a	yield[c] (%) 6b
1	**1a**	7.1	none	4	90.9	
2	**1a**	7.1	PDNB (0.181)[d]	4	26.7	
3	**1a**	6.9	MDNB (0.263)[e]	4	61.0	
4	**1a**	7.1	ODNB (0.312)[f]	4	14.1	
5	**1b**	7.2	none	2	87.2	
6	**1b**	7.3	PDNB (0.246)	2	31.9	
7	**1b**	7.0	MDNB (0.326)	2	57.6	
8	**1b**	7.0	ODNB (0.244)	2	41.7	
9	**1c**	7.0	none	0.5		98.7
10	**1c**	7.1	PDNB (0.268)	0.5		0
11	**1c**	7.0	MDNB (0.296)	0.5		10.9
12	**1c**	7.1	ODNB (0.280)	0.5		7.5
13	**1d**	6.7	none	4		76.5
14	**1d**	7.0	PDNB (0.360)	4		3.7
15	**1d**	7.3	MDNB (0.346)	4		76.0
16	**1d**	7.0	ODNB (0.295)	4		13.5
17	**1e**	7.1	none	4		83.1
18	**1e**	7.0	PDNB (0.187)	4		5.6
19	**1e**	7.2	MDNB (0.342)	4		14.4
20	**1e**	7.1	ODNB (0.258)	4		4.5
21	**1f**	7.0	none	4		94.5
22	**1f**	7.0	none	2		66.4
23	**1f**	9.0	PDNB (0.248)	2		15.5
24	**1f**	7.0	MDNB (0.309)	2		17.6
25	**1f**	7.2	ODNB (0.218)	2		16.7

[a] Reaction conditions: DMSO (solvent); temperature 90 ± 1 °C; initial concentration $[1]_0$ ca. 0.005 M. [b] Molar ratios were calculated on the basis of **1**. [c] Yields of the products were calculated on the basis of **1**. [d] PDNB = *p*-dinitrobenzene. [e] MDNB = *m*-dinitrobenzene. [f] ODNB = *o*-dinitrobenzene.

Scheme II

$$\begin{array}{lll}
ArX + e \longrightarrow ArX^{\bar{\cdot}} & & \text{Initiation} \\
ArX^{\bar{\cdot}} \longrightarrow Ar^{\cdot} + X^- & \left.\begin{array}{l} \\ \\ \\ \end{array}\right\} & \\
Ar^{\cdot} + Nu^- \longrightarrow ArNu^{\bar{\cdot}} & & \text{Propagation} \\
ArNu^{\bar{\cdot}} + ArX \longrightarrow ArNu + ArX^{\bar{\cdot}} & & \\
\hdashline
ArX + Nu^- \longrightarrow ArNu + X^- & &
\end{array}$$

reactive or less stable than the other *p*-nitrohalobenzene radical anions. A possible reason for the discrepancy is the involvement of the counterion (Na^+) in the transition state of the dissociation reactions of the radical anion intermediates **3** (Scheme I). The interaction of the fluorine in **3c** with the counterion (Na^+) in the solvent cage is much stronger than the other haloatoms in **3** with the counterion (Na^+) since Na^+ ion is a hard acid and F^- ion is the hardest base known. The idea of the involvement of the counterion (Na^+) in the transition state of the dissociation reactions of the *o*- and *p*-nitrohalobenzene radical anions is supported by the observations that all of the activation entropies for the dissociation reactions of **3a**, **3d**, and **3e** determined in the reactions of **1a**, **1d**, and **1e** with **2**, respectively, are large and negative.[10] It is reasonable since the oxidation potentials of anions have been found to be highly dependent on the nature of the counterions present in solution.[19]

Examination of Table II indicates that the relative reactivities for the reactions of *p*-nitrohalobenzenes with **2** are in the following order: **1c** (p-$NO_2C_6H_4F$) ≫ **1f** (p-$NO_2C_6H_4I$) > **1e** (p-$NO_2C_6H_4Br$) > **1d** (p-$NO_2C_6H_4Cl$). This trend is the same as that observed for the reactions of *p*-nitrohalobenzenes with various anions as reported by Bordwell and Hughes[6c] but is in sharp contrast to the order ArF ≫ ArCl ≥ ArBr ≥ ArI reported for the polar nucleophilic substitution reaction (S_NAr) and to the order ArI > ArBr > ArCl > ArF reported for the $S_{RN}1$ reaction.[17]

The higher reactivities of the ortho isomers (**1a** and **1b**) than the corresponding para isomers (**1d** and **1e**) are consistent with the faster fragmentation rate constants of the *o*-nitrohalobenzene radical anions than those of the corresponding *p*-nitrohalobenzene radical anions,[18] presumably due to the steric inhibition of the coplanarity of the nitro group with the aromatic ring by the adjacent C–X bonds in the ortho isomers and the direct transfer of the electron from the nitro group to the σ^* orbital of the C–X bonds.

Effects of the Radical Scavengers on the Reactions of *o*- and *p*-Nitrohalobenzenes with the Sodium Salt of Ethyl α-Cyanoacetate Carbanion. The effects of galvinoxyl, 2-methyl-2-nitrosopropane dimer [$(t\text{-BuN=O})_2$], phenyl *tert*-butyl nitrone, 4-ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl, and hydroquinone on the reactions of **1** with **2** are summarized in Table III.

The inhibition of radical scavengers has been suggested as one of the criteria for the assignment of the $S_{RN}1$ mechanism.[17] Galvinoxyl and nitroxyl radicals are common radical scavengers used to test for the $S_{RN}1$ reaction.[2d] Nitroso and nitrone compounds are also common radical trapping reagents.[20] Examination of Table III reveals that addition of the five radical scavengers to the reactions of **1** with **2** in DMSO did not appreciably lower the yields of the products **6**. The quantities of the radical scavengers used were well sufficient in general to depress severely the $S_{RN}1$ chain propagation.[2d] The observation of little or no retardation effects by radical scavengers definitely rules out the possibility that the reactions of **1** with **2** proceed via the $S_{RN}1$ mechanism (Scheme II) since the radical scavengers can trap the free-radical intermediates (the chain carriers) and dramatically depress the $S_{RN}1$ reactions.[2,15,17]

The failure of the radical scavengers to affect the yields of the reactions of **1** with **2** (Table III) can be rationalized by the nonchain radical mechanism (Scheme I) since the reactive radical intermediates are held within the solvent cage which the radical scavengers evidently cannot penetrate the solvent cage as electron. In other words, the radicals in nonchain radical mechanism are free to be

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Table III. Effects of the Radical Scavengers on the Reactions of *o*- and *p*-Nitrohalobenzenes (1) with $Na^{+-}CH(CN)CO_2Et$ (2) in DMSO[a]

no.	substrate	$[2]_0/[1]_0$	scavengers (molar ratio)[b]	time (h)	yield[c] (%) 6a	yield[c] (%) 6b
1	**1a**	7.1	none	4	90.9	
2	**1a**	7.0	GAL (0.217)[d]	4	91.2	
3	**1a**	7.2	MND (0.601)[e]	4	78.8	
4	**1a**	7.1	PBN (0.295)[f]	4	87.0	
5	**1a**	7.0	TMP (0.290)[g]	4	88.4	
6	**1b**	7.2	none	2	87.2	
7	**1b**	7.2	GAL (0.232)	2	88.7	
8	**1b**	7.0	MND (0.604)	2	77.4	
9	**1b**	7.0	PBN (0.272)	2	83.1	
10	**1b**	7.1	TMP (0.321)	2	86.5	
11	**1c**	7.0	none	0.5		98.7
12	**1c**	7.1	GAL (0.255)	0.5		93.0
13	**1c**	6.9	MND (0.492)	0.5		93.2
14	**1c**	7.0	PBN (0.339)	0.5		95.9
15	**1c**	7.2	TMP (0.321)	0.5		95.7
16	**1d**	6.7	none	4		76.0
17	**1d**	7.0	GAL (0.281)	4		74.0
18	**1d**	7.1	MND (0.402)	4		69.1
19	**1d**	6.9	PBN (0.280)	4		75.5
20	**1d**	7.1	HYD (0.472)[h]	4		70.6
21	**1d**	7.0	TMP (0.310)	4		74.5
22	**1d**	112	none	4		100
23	**1d**	120	GAL (0.280)	4		100
24	**1d**	110	MND (0.702)	4		99.5
25	**1d**	125	PBN (0.651)	4		100
26	**1d**	115	TMP (0.350)	4		100
27	**1e**	7.1	none	4		83.1
28	**1e**	7.1	GAL (0.261)	4		78.7
29	**1e**	6.8	MND (0.540)	4		74.6
30	**1e**	7.0	PBN (0.362)	4		84.6
31	**1f**	7.0	none	2		66.4
32	**1f**	7.0	GAL (0.176)	2		57.7
33	**1f**	6.9	MND (0.445)	2		53.7
34	**1f**	6.9	PBN (0.293)	2		60.2
35	**1f**	7.1	TMP (0.335)	2		65.1

[a] Reaction conditions: DMSO (solvent); temperature 90 ± 1 °C; initial concentration $[1]_0$ ca. 0.005 M. [b] Molar ratios were calculated on the basis of **1**. [c] Yields of the products were calculated on the basis of **1**. [d] GAL = galvinoxyl. [e] MND = 2-methyl-2-nitrosopropane dimer. [f] PBN = phenyl *tert*-butyl nitrone. [g] TMP = 4-ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl. [h] HYD = hydroquinone.

trapped by the radical scavengers present in the solution. The little or no inhibition effects by radical scavengers have been observed for several SET reactions in the literature.[21-24] For example, Russell and Ros have found that the radical nucleophilic substitution reaction of 1,1-dimethyl-*p*-nitrophenacyl chloride with the potassium salt of ethyl α-cyanoacetate carbanion in DMSO or DMF was not affected by addition of radical scavengers such as $(t\text{-Bu})_2NO^{\bullet}$ or galvinoxyl, but no explanation was given.[21b]

Comparison of entry 22 with entry 16 in Table III shows that the product yields of **1d** with **2** are highly dependent on the initial concentrations. This is consistent with the second-order kinetics.[10] There was also no observable inhibition by the radical scavengers on the reaction of **1d** with **2** even in the presence of a great excess (more than 100-fold) of the radical scavengers.

Experimental Section

Materials. *m*-Dinitrobenzene, hydroquinone, dimethyl sulfoxide (DMSO), ethyl α-cyanoacetate, and galvinoxyl were commercially available and were used as received unless otherwise indicated. *p*-Dinitrobenzene,[25] *o*-dinitrobenzene,[25], 4-ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl,[26] 2-methyl-2-nitrosopropane dimer,[27] and phenyl-*tert*-butylnitrone[28] were synthesized according to the literature methods.

Ethyl α-cyanoacetate was dried over anhydrous calcium chloride for 1 day and then distilled under reduced pressure. DMSO was dried over anhydrous potassium hydroxide for 1 day and distilled from powdered calcium hydride under reduced pressure. Sodium hydride (containing ca. 20% mineral oil) was made oil free by three extractions with petroleum ether followed by decanting the supernatant. The preparation of the sodium salt of ethyl α-cyanoacetate carbanion (**2**) and the determination of the content in the products have been described previously.[10b] Ethyl α-cyano-α-(*o*-nitrophenyl)acetate (**6a**) and ethyl α-cyano-α-(*p*-nitrophenyl)acetate (**6b**) were prepared and purified as described previously.[10]

Electrochemistry. The redox potentials of dinitrobenzenes (PDNP, MDNP, ODNP) and *o*- and *p*-nitrohalobenzenes were measured in DMSO with 0.1 M tetraethylammonium tetrafluoroborate as supporting electrolyte by cyclic voltammetry using a Princeton P & PAC Potentiostat analysis electrometer. The working and auxiliary electrodes were platinum, and the reference electrode was a saturated calomel electrode (SCE). The scan rate was 100 mV/s. All the electrochemical experiments were carried out under an argon atmosphere.

Quantitative Determination of the Product Yields. The reaction flasks which contained the exact amounts of **1**, **2**, and the electron acceptors or radical scavengers were kept in a thermostat (90 ± 1 °C) for a definite period of time, and then the reactions were quenched with glacial acetic acid. After cooling to the room temperature, the reaction mixtures were diluted to a certain volume and analyzed with Gilson HPLC (UV-visible detector, ODS-18 reversed-phase column) with a mixed solvent of water and methanol (v:v, 40:60) as the eluant.

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