J. Org. Chem. **1993,** *58,* 7350–7354

Kinetic and Mechanistic Studies of the Nonchain Radical Nucleophilic Substitution Reactions

Xian-Man Zhang,*,† Di-Lun Yang, Xue-Qing Jia, and You-Cheng Liu

The National Laboratory of Applied Organic Chemistry and Chemistry Department, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

Received July 16, 1993●

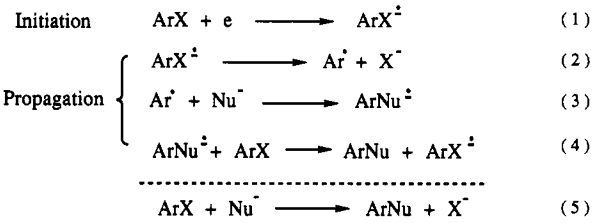
The kinetics of the radical nucleophilic substitution reaction of *p*-nitrochlorobenzene with the sodium salt of the ethyl α-cyanoacetate carbanion in dimethyl sulfoxide (DMSO) solution at 335.9, 340.1, 343.9, 347.7, and 351.4 K were determined by observing the increase of the UV-visible absorbance of the product, the ethyl α-cyano-α-(*p*-nitrophenyl)acetate carbanion. The activation energies and entropies for the single electron transfer (k_1) and for the *p*-nitrochlorobenzene radical anion dissociation (k_2) were obtained. These results strongly support the previous conclusion that the thermal nucleophilic substitution reactions of *o*- and *p*-nitrohalobenzenes with the sodium salt of ethyl α-cyanoacetate carbanion in DMSO solution proceed exclusively via a nonchain radical mechanism (Scheme II).

Introduction

Aromatic nucleophilic substitution reactions stimulated by photoradiation, solvated electrons, or at electrodes, are believed to proceed via a chain radical unimolecular mechanism ($S_{RN}1$) as shown in Scheme I.[1] The initial step (eq 1) is the formation of an aromatic halide radical anion ($ArX^{\cdot-}$) by addition of a solvated electron or an electron derived from a nucleophile or at an electrode to an aryl halide. Addition of one electron to a molecule usually results in an increase of its reactivity because the bond dissociation energies in radical anions were shown to be much smaller than those in the corresponding neutral molecules.[2] The second step is the dissociation of the aryl halide radical anion ($ArX^{\cdot-}$) to form the aryl radical ($Ar^{\cdot}$) and the halide ion (X^-). The aryl radical then combines with the nucleophile (Nu^-) to generate the product radical anion ($ArNu^{\cdot-}$) which, in turn, transfers one electron to the starting material (ArX) to yield the product (ArNu) and a radical anion ($ArX^{\cdot-}$) to continue the chain.[3]

The chain radical mechanism ($S_{RN}1$) has been widely accepted because it is supported by numerous experimental results including (i) significant catalysis by photoradiation, or by solvated electrons, or by electrons at electrodes,[1a–g] (ii) inhibition by addition of a catalytic amount of an electron acceptor or radical scavenger,[1a–f] (iii) chain lengths that are longer than one,[4a–c] (iv) insensitivity to steric effects,[1h,i] and (v) complex kinetics.[4b,d,e]

Scheme I



$$ArX + e \longrightarrow ArX^{\cdot-} \qquad (1)$$

$$ArX^{\cdot-} \longrightarrow Ar^{\cdot} + X^- \qquad (2)$$

$$Ar^{\cdot} + Nu^- \longrightarrow ArNu^{\cdot-} \qquad (3)$$

$$ArNu^{\cdot-} + ArX \longrightarrow ArNu + ArX^{\cdot-} \qquad (4)$$

$$ArX + Nu^- \longrightarrow ArNu + X^- \qquad (5)$$

Bunnett suggested that the dissociation of the halide radical anions (eq 2) in $S_{RN}1$ reactions follows a unimolecular process.[1a,3c] But the activation entropies determined for the dissociation reactions for various halide radical anions have been found to be large and negative values (<–20 eu) under similar experimental conditions reported for $S_{RN}1$ reactions, suggesting that the dissociation reactions of halide radical anions do not follow a unimolecular mechanism, but instead follow a bimolecular mechanism.[5]

In addition, many radical reactions labeled as $S_{RN}1$ reactions were reported to give quantitative yields (100%).[6] These observations are not consistent with the diffusion-controlled or near diffusion-controlled hydrogen abstraction by aryl radicals from the solvents used for most $S_{RN}1$ reactions.[7] Note also that the concentration of the solvent used is generally much larger than that of the nucleophile. The coupling reaction of two aryl radicals was suggested

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† To whom the correspondence should be addressed at the Chemistry Department of Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113.

● Abstract published in *Advance ACS Abstracts,* December 1, 1993.

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(3) The $S_{RN}1$ mechanism was first independently proposed by Kornblum[3a] and Russell.[3b] But the $S_{RN}1$ nomenclature was suggested by Bunnett,[3c] where S is substitution, N is nucleophilic, R is radical, and 1 is unimolecular. Bordwell[3d] has objected to this nomenclature because it implies that the dissociation, i.e. step 2, is rate determining. They have argued that step 2 is least likely to be rate-determining. (a) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966,** *88,* 5662. (b) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966,** *88,* 5663. (c) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970,** *92,* 7463. *Ibid.* **1970,** *92,* 7464. (d) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1982,** *47,* 2510.

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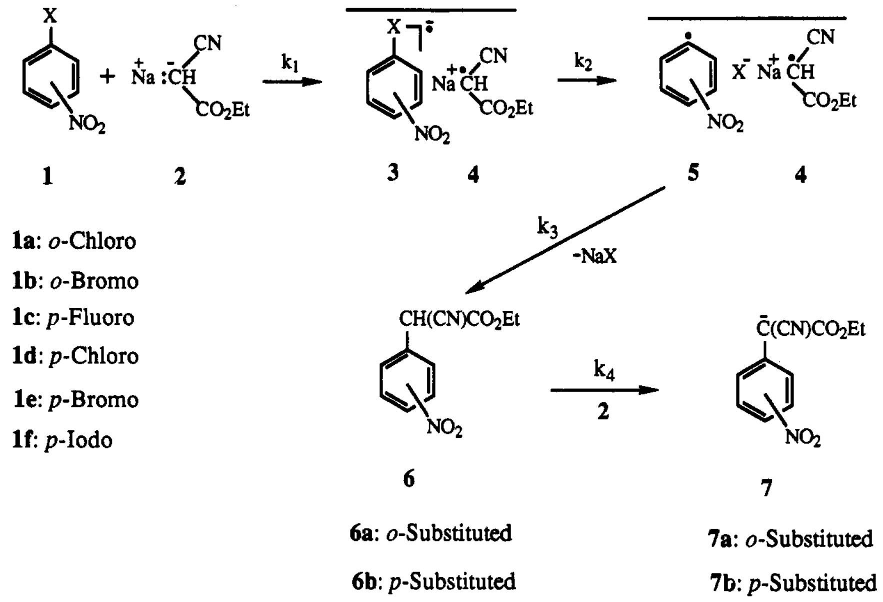
Scheme II



as one of the possible termination steps for the $S_{RN}1$ reaction.[1a–d,8] But no dimer derived from such coupling reactions among the reaction products of the reported $S_{RN}1$ reactions under various experimental conditions has ever been found in amounts large enough to be detected by ordinary analytical techniques.[8] Also no inhibition or only partial inhibition effects on many radical nucleophilic substitution reactions have been observed by addition of different radical scavengers.[4b,e,9,12,13] These experimental observations are clearly not consistent with the $S_{RN}1$ mechanism, indicating that many radical nucleophilic substitution reactions labeled as $S_{RN}1$ mechanism in the literature do not proceed via the chain radical mechanism, but probably proceed via a nonchain radical mechanism.[10–12] However, recently, the reality of the $S_{RN}1$ reaction mechanism has been questioned by Denney,[13] but was rebutted by Bunnett[14] and by Rossi.[15]

We have proposed a nonchain radical nucleophilic substitution mechanism for the thermal reactions of *o*- and *p*-nitrohalobenzenes **1** with the sodium salt of the ethyl α-cyanoacetate carbanion (**2**) in dimethyl sulfoxide (DMSO) solution as shown in Scheme II.[12] The first step is the formation of electron donor–acceptor complex followed by a single electron transfer (SET) reaction to form a radical anion (**3**) and radical cation (**4**) complex. The reactions directed to the final products will then be completed within a solvent cage.

The reactions of **1** with **2** in DMSO gave strong ESR spectra of the *o*- and *p*-nitrohalobenzene radical anions (**3**). UV-visible spectra of the electron donor–acceptor complexes were also seen, and broadening effects on the NMR absorption peaks of **1** were also observed.[12b,d] The reactions were found to be significantly inhibited by addition of catalytic amounts of strong electron acceptors such as dinitrobenzenes, but were not affected by addition of different radical scavengers such as galvinoxyl, even in large excess.[12a] Dioxygen also has no effect on these radical reactions.[12d] Furthermore, the nonchain radical mechanism was supported by the kinetic studies on the radical anion reactive intermediates **3** determined by the ESR field/frequency lock technique.[16] The activation parameters of *o*-nitrochlorobenzene radical anion (**3a**), *p*-nitrochlorobenzene radical anion (**3d**), and *p*-nitrobromobenzene radical anion (**3e**) derived from the reactions of **1a**, **1d**, and **1e** with **2**, respectively, were determined.[12b,c] It appeared to be of interest to investigate further the kinetics for the product formation and to check the results obtained on the radical intermediates. In the present paper, we report kinetic results obtained by probing the UV-visible absorption peak of the ethyl α-cyano-α-(*p*-nitrophenyl)-acetate carbanion (**7b**), the product anion formed in the reaction of **1d** with **2** in DMSO solution, at different temperatures. The reason for this choice was the fact that reaction of **1d** with **2** is slow enough, so that it can be easily studied at various temperatures in the 50–80 °C range.

Results and Discussion

Both the UV-visible spectra of **1d** and **2** in DMSO solution are transparent in the range >400 nm, but **7b** has a strong absorption peak at $\lambda_{max} = 498$ nm ($\epsilon_{max} > 10^4$). The kinetic measurements for the **7b** formation in the reaction of **1d** with **2** were probed at wavelengths of 498, 510, and 525 nm for five different temperatures. The

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[8] Page 241 of ref 1c.

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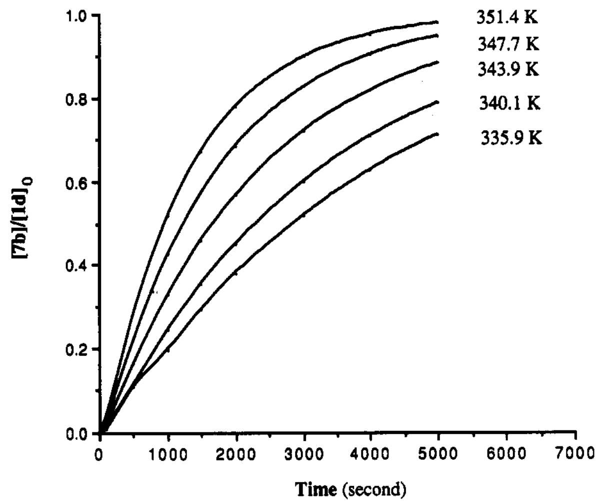

Figure 1. Plots of the relative concentration ratios [**7b**]/[**1d**]$_0$ versus time for the reaction of **1d** with **2** in different temperatures.

kinetic curves obtained by probing at 498 nm for five different temperatures are shown in Figure 1.

Radical–radical coupling reactions are very rapid, usually in the diffusion-controlled or near diffusion-controlled range. The proton exchange reaction of **6b** with **2** should be very fast because **6b** is about 10 pK_{HA} units more acidic than the conjugate acid of **2** in DMSO solution.[17] It is reasonable to assume that the coupling reaction of *p*-nitrophenyl radical (**5d**) with (ethoxycarbonyl)cyanomethyl radical (**4**) and the deprotonation reaction of ethyl α-cyano-α-(*p*-nitrophenyl)acetate (**6b**) by base **2** are both much faster than the single electron transfer reaction (k_1) and the dissociation reaction of the *p*-nitrochlorobenzene radical anion (k_2), i.e. $k_1, k_2 << k_3, k_4$.[12b–d] In other words, the first two steps (k_1 and k_2) are the rate-determining steps for the reaction of **1d** with **2** as shown in Scheme II. Then the reaction of **1d** with **2** in DMSO can be simply expressed as eq 6 because the overall reaction rate is controlled by the rate-determining steps.

$$\mathbf{1d} + \mathbf{2} \xrightarrow{k_1} \mathbf{3d} \xrightarrow{k_2} \mathbf{7b} \qquad (6)$$

In earlier studies,[12b–d] we have shown that under the pseudo-first-order conditions, the ratios of the maximum concentration of **3d** with the initial concentration of **1d**, [**3d**]$_{max}$/[**1d**]$_0$ are all smaller than e^{-1} (~0.368) in the temperature range of 50–100 °C, indicating that k_1 is smaller than k_2, i.e. the first step is the rate-determining step for the reaction of **1d** with **2** according to the e^{-1} criterion.[18] Therefore, the rate constants k_1 and k_2 can be determined by using eq 7.[19]

$$\frac{[\mathbf{7b}]}{[\mathbf{1d}]_0} = \left(1 - \frac{k_2'}{k_2' - k_1'} e^{-k_1' t} + \frac{k_1'}{k_2' - k_1'} e^{-k_2' t}\right) \qquad (7)$$

where $k_1' = k_1 \times [\mathbf{2}]_0$ and $k_2' = k_2 \text{ x } [\mathbf{2}]_0$.

The apparent rate constants at different temperatures were calculated by using a computer simulation program designed on the basis of eq 7,[20] and the results are summarized in Table I. The calculated rate constants from the measurements at wavelengths of 498, 510, and 525 nm were shown to be identical within experimental error, indicating that the weak absorption of the electron donor–acceptor complexes near 420 nm (ϵ_{max} = ~1000) did not interfere with the kinetic measurements of the product anion formation.[12b,d]

Table I. Apparent and Absolute Rate Constants of the First Two Steps for Reaction of 1d with 2[a]

temp (K)	335.9	340.1	343.9	347.7	351.4
k_1' (s^{-1})[b]	2.55×10^{-4}	3.17×10^{-4}	4.35×10^{-4}	5.97×10^{-4}	7.78×10^{-4}
k_2' (s^{-1})[b]	7.80×10^{-3}	8.97×10^{-3}	1.19×10^{-2}	1.34×10^{-2}	1.56×10^{-2}
k_1 (M^{-1} s^{-1})[c]	6.26×10^{-4}	7.77×10^{-4}	1.07×10^{-3}	1.46×10^{-3}	1.91×10^{-3}
k_2 (M^{-1} s^{-1})[d]	1.92×10^{-2}	2.20×10^{-2}	2.92×10^{-2}	3.29×10^{-2}	3.83×10^{-2}
ϵ[e]	3.21×10^{4}	3.16×10^{4}	3.09×10^{4}	2.98×10^{4}	2.88×10^{4}

[a] Reaction conditions: [**1d**]$_0$ = 3.55×10^{-5} M, [**2**]$_0$ = 0.407 M in DMSO solution. [b] Apparent rate constants. [c] $k_1 = k_1'/[\mathbf{2}]_0$. [d] $k_2 = k_2'[\mathbf{2}]_0$. [e] ϵ = extinction coefficients of the ethyl α-cyano-α-(*p*-nitrophenyl)acetate carbanion.

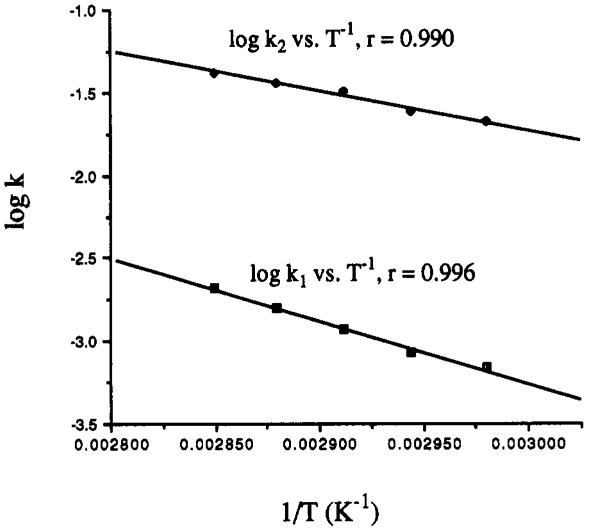

Figure 2. Plots of log k vs T^{-1} for step 1 (single electron transfer reaction) and step 2 (*p*-nitrochlorobenzene radical anion dissociation) for the reaction of **1d** with **2** in DMSO solution.

Table II. Activation Energies and Activation Entropies for Step 1 and Step 2 for the Reaction of 1d with 2 in DMSO Solution

reaction	E_a[c]	ΔS_{298}[d]	r[e]	ref
step 1 (k_1)[a]	73 [illegible] 3	−91 ± 4	0.996	this work
step 1 (k_1)[a]	75 ± 3	−94 ± 4	0.999	12b
step 2 (k_2)[b]	45.5 ± 3	−144 ± 6	0.990	this work
step 2 (k_2)[b]	54 ± 5	−135 ± 6	0.998	12b

[a] Single electron transfer reaction. [b] Dissociation reaction of *p*-nitrochlorobenzene radical anion. [c] In kJ mol^{-1}; activation energies. [d] In J K^{-1} mol^{-1}; activation entropies. [e] Correlation coefficient.

Figure 2 shows that the Arrhenius empirical plots of log k vs $1/T$ are excellent straight lines for both the reactions of steps 1 and 2. The activation energies and activation entropies obtained therefrom are summarized in Table II. The activation energies and entropies obtained from the measurements by means of the ESR F/F lock technique on the radical anion intermediates are also included for comparison. Examination of Table II shows that the activation entropies for the step 2 reaction, the dissociation

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Table III. Relationship of the Apparent Rate Constants with the Concentration of 2[a]

$[2]_0$ (M)	2.72×10^{-2}	2.04×10^{-1}	4.07×10^{-1}
k_1' (s^{-1})	3.28×10^{-5}	2.27×10^{-4}	4.35×10^{-4}
k_1 ($M^{-1}\,s^{-1}$)[b]	1.21×10^{-3}	1.11×10^{-3}	1.07×10^{-3}
k_2' (s^{-1})	8.65×10^{-4}	6.20×10^{-3}	1.19×10^{-2}
k_2 ($M^{-1}\,s^{-1}$)[c]	3.18×10^{-2}	3.04×10^{-2}	2.92×10^{-2}

[a] Reaction conditions: $[\mathbf{1d}]_0 = 3.55 \times 10^{-5}$ M, temperature = 343.9 K in DMSO solution. [b] $k_1 = k_1'/[2]_0$. [c] $k_2 = k_2'[2]_0$.

Table IV. Effects of Radical Scavengers on the Reaction of 1d with 2[a]

radical scavengers	molar ratio[d]	cage effects,[e] %	k_1, $M^{-1}\,s^{-1}$	k_2, $M^{-1}\,s^{-1}$
none			1.46×10^{03}	3.29×10^{-2}
MND[b]	118	98	1.47×10^{-3}	3.22×10^{-2}
TMP[c]	178	98	1.47×10^{-3}	3.15×10^{-2}
TMP[c]	1850	96	1.52×10^{-3}	3.05×10^{-2}

[a] Reaction conditions: $[\mathbf{1d}]_0 = 3.55 \times 10^{-5}$ M, temperature = 347.7 K in DMSO solution. [b] MND = 2-methyl-2-nitrosopropane dimer. [c] TMP = 4-ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl. [d] Molar ratio = [radical scavenger]/$[\mathbf{1d}]_0$. [e] Cage effects are defined by the ratios of the concentration of the product anion ([**7b**]) in the presence and absence of radical scavengers, which were determined by the UV-visible spectrophotometer in the same time under the same reaction conditions.

of *p*-nitrochlorobenzene radical anion, obtained from two different methods are all large and negative values (~ −32 eu), suggesting that the dissociation of the *p*-nitrochlorobenzene radical anion does not follow the unimolecular process, but follows a bimolecular process.[5] The counterion (Na^+) was believed to be involved in the transition state of the dissociation of *o*- and *p*-nitrohalobenzene radical anions.[12] The remarkable agreement of the kinetic results obtained from the measurements on the radical anion intermediates by the ESR F/F lock technique and on the product anion by the UV-visible spectrophotometric method strongly supports the conclusion that the thermal reactions of **1** with **2** in DMSO solution proceed exclusively via the nonchain radical mechanism (Scheme II).

It is seen from an inspection of Table III that the apparent rate constants (k_1' and k_2') are linearly proportional to the concentration of **2**, but the absolute rate constants (k_1 and k_2) calculated (Table III) are independent, within experimental error, on the concentrations of **2**. These results are not unexpected because the rate-determining steps of the nonchain radical reactions as shown (Scheme II) follow the second-order reaction mechanisms.

In earlier studies,[12a,b] we have found that addition of radical scavengers such as galvinoxyl, do not affect the substitution product yields for the thermal radical reactions of **1** with **2** in DMSO solution. Examination of Table IV shows that addition of radical scavengers such as 2-methyl-2-nitrosopropane dimer (MND) and 4-ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl (TMP) also have no effect on the rate constants for the reaction of **1d** with **2**, even after addition of a large excess of radical scavengers (more than 1000 times). These results are not surprising because the radical reaction of **1d** with **2** in DMSO occurs exclusively in the solvent cage, and the radical scavengers can not penetrate the solvent cage wall and trap the radical intermediates.[12a] Note that the cage effects for this reaction was also determined to be larger than 95% (Table IV).

It is interesting to know that the extinction coefficient (ε) of the ethyl α-cyano-α-(*p*-nitrophenyl)acetate carbanion in DMSO (Table I) decreases progressively as the reaction temperature increases. This is not difficult to understand because molecular movement is expected to increase as the temperature increases, and this will definitely result in the broadening of the UV-visible absorption peaks and decrease the extinction coefficient. But the magnitude of the extinction coefficients also can be linearly correlated with the reaction temperature as shown in Figure 3.

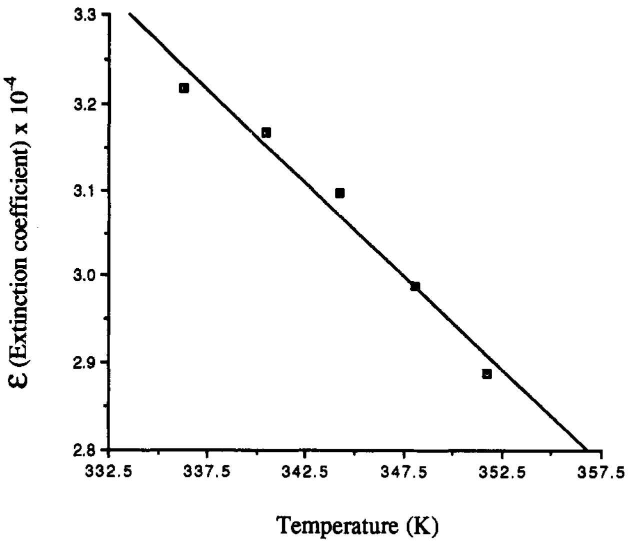

Figure 3. Linear plot for the extinction coefficients (ε) of the ethyl α-cyano-α-(*p*-nitrophenyl)acetate carbanion in DMSO solution versus the reaction temperature.

Experimental Section

Materials: Dimethyl sulfoxide (DMSO) and ethyl α-cyanoacetate were commercially available samples. 4-Ethoxy-2,2,6,6-tetramethylpiperidine nitroxyl[20] and 2-methyl-2-nitrosopropane dimer[21] were synthesized according to 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 then 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 mixture have been described previously.[12b] Ethyl α-cyano-α-(*p*-nitrophenyl)acetate (**6b**) was prepared and purified as described previously.[12b,c]

Kinetic Measurements. Under an argon atmosphere, the DMSO solutions of **1d**, **2**, and radical scavenger (if needed) were mixed in the UV cell (1 cm) and quickly placed in a temperature-controlled (± 0.1 °C) Shimadzu UV-visible spectrophotometer. The reaction temperature was corrected periodically with a standard thermometer. The kinetic measurements for the **7b** formation were followed under pseudo-first-order reaction conditions with a large excess of **2** by observing the increase in the intensity at 498, 510, and 525 nm for different temperatures. Checks have been made to confirm that more than 90% of the starting material (ArX) was usually converted into the product anion (**7b**) for each measurement. The rate constants were calculated by a least-squares curve fitting computer program.[20]

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Appendix

For a first-order successive reaction (eq 8):

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (8)$$

Equation 9 can be derived for the above reaction.[19]

$$\frac{[B]_{max}}{[A]_0} = m^{m/1-m} \qquad (9)$$

where $[B]_{max}$ is the maximum concentration of the intermediate B, $[A]_0$ is the initial concentration of starting material A, and $m = k_2/k_1$.

Equation 9 shows that the ratio of rate constant k_1 and k_2 is only dependent on the ratio of the maximum concentration of **B** ($[B]_{max}$) to the initial concentration of **A** ($[A]_0$), both of which are experimentally measurable. Analysis of eq 9 also indicates that they have the following relationship, called the e^{-1} criterion.[17b] (i) If $[B]_{max}/[A]_0 < e^{-1} \approx 0.368$, the m should be larger than 1, i.e., k_1 is smaller than k_2. Therefore, the first step (k_1) is the rate-determining step. (ii) If $[B]_{max}/[A]_0 > e^{-1} \approx 0.368$, the m should be smaller than 1, i.e. k_1 is larger than k_2. Therefore, the second step (k_2) is the rate-determining step. (iii) If $[B]_{max}/[A]_0 = e^{-1} \approx 0.368$, the m should be equal to 1, i.e. k_1 is equal to k_2. There is no rate-determining step.

Acknowledgment. This research was supported by the National Natural Science Foundation of People's Republic of China.