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Aromatic Nucleophilic Substitution. XVI.[1] Stopped-flow Kinetics of Formation and Decomposition of 1,3- and 1,1-Disubstituted Anionic σ Complexes in Reactions of 1-Dimethylamino-2,4-dinitronaphthalene with Potassium Alkoxides in Dimethyl Sulfoxide–Alcohol

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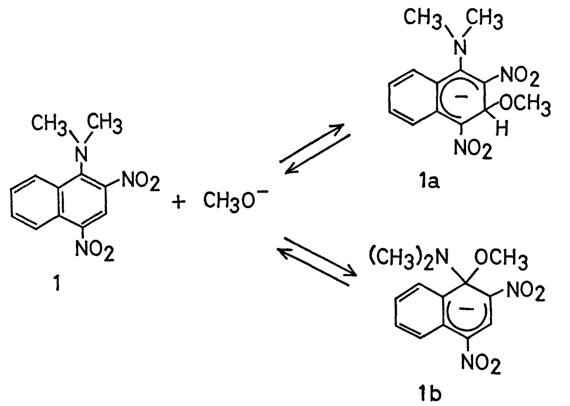
Reactions of 1-dimethylamino-2,4-dinitronaphthalene with potassium methoxide or ethoxide were carried out in DMSO–CH_3OH or DMSO–C_2H_5OH (90:10 v/v), respectively, where the 1,3-disubstituted anionic σ complexes were first rapidly formed, undergoing isomerizations to the 1,1-disubstituted anionic σ complexes. Rates and activation parameters were determined by kinetic studies using stopped-flow and conventional spectrophotometers. The rate constant (25 °C) for the formation of 1,3-disubstituted one in DMSO–CH_3OH is about half that in DMSO–C_2H_5OH, whereas the rate constant (25 °C) for its decomposition is more than twice that in DMSO–C_2H_5OH. The apparent pseudo-first-order rate constant for the formation of 1,1-disubstituted anionic σ complex in DMSO–CH_3OH depends upon the methoxide ion concentration, whereas that in DMSO–C_2H_5OH is almost independent of the ethoxide ion concentration. The mechanism is discussed on the basis of activation parameters.

In our previous work[1] we reported detailed kinetics of reactions of 1-dialkylamino-2,4-dinitronaphthalenes with potassium methoxide in DMSO–CH_3OH, where 1,3-disubstituted anionic σ complexes are first formed, undergoing isomerizations to 1,1-disbustituted ones according to



(1a)

(1b)

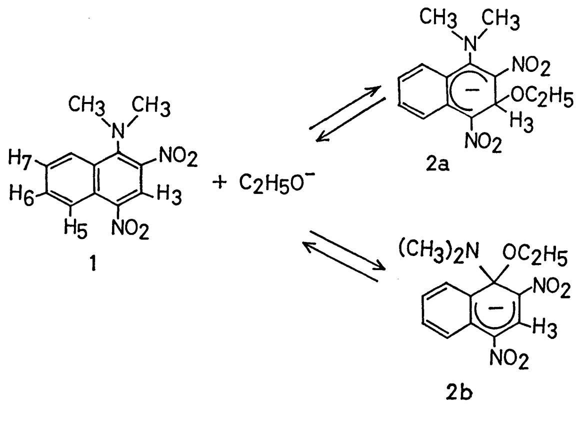
Thus we found that the kind of the 1-dialkylamino groups and the DMSO content in the mixed solvent will affect the rate of formation and decomposition of 1,3- (**1a**) and 1,1-disubstituted anionic σ complexes (**1b**).

Therefore, replacement of potassium methoxide by potassium ethoxide would be expected to affect the rates of formation and decomposition of both complexes.

This paper reports a comparison of the results obtained in the case of potassium ethoxide with those in the case of potassium methoxide in order to elucidate further the reaction mechanism.

Results

Absorption Spectra. Upon addition of excess ethanolic C_2H_5OK to 1-dimethylamino-2,4-dinitronaphthalene (**1**) in DMSO–C_2H_5OH (90:10 v/v), the solution was colored red instantly (Fig. 1): Curve b, for the formation of a complex (**2a**, corresponding to **1a**), was first obtained, which was then gradually changed into Curve d due to the formation of a complex (**2b**, corresponding to **1b**). The time-dependent spectral change is clearly interpreted on the basis of the reaction paths defined by



(2a)

(2b)

On the other hand, NMR spectrometry, which is generally recognized useful for elucidating structures of anionic σ complexes,[2,3] also showed that the process (Eq. 2) is valid: Just after addition of ethanolic C_2H_5OK (1.19×10^{-4} mol) to a DMSO solution (0.4 ml) of **1** (1.15×10^{-4} mol) at room temperature, the solution turned red at once, suggesting the formation of a complex. Just after addition, H_3 sharp singlet (δ=8.70) of **1** shifted upfield (δ=6.27, H_3 of **2a**). Fast sweep time (500 Hz/50 s) and fast procedures are indispensable for detecting spectral changes. One minute and a half after addition, a new singlet, due to H_3 of **2b**, appeared at δ=9.26 at the expense of the singlet at δ=6.27 which appeared faintly.

It is thus expected that the discrete kinetics of formation and decomposition of **2a** and **2b** is possible.

Kinetic Runs. Let us rewrite Eq. 2 in a form convenient for quantitative discussion as follows:

$$\mathbf{1} + C_2H_5O^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{2a}, \qquad (3a)$$

$$\mathbf{1} + C_2H_5O^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathbf{2b}, \qquad (3b)$$

$$K_1 = \frac{k_1}{k_{-1}},\ K_2 = \frac{k_2}{k_{-2}}.$$

According to the results of UV-VIS and NMR spectra, the reaction will occur in two distinct stages: The chemical transformations responsible for the first (Spectrum a→b) and second spectral changes (Spectrum b→c→d), to be termed Stage I and Stage II, respectively. The Stage I reaction ($\mathbf{1}\rightleftarrows\mathbf{2a}$) is much faster than the Stage II reaction ($\mathbf{1}\rightleftarrows\mathbf{2b}$). Accordingly, in treating the Stage I kinetics, the Stage II reaction can be neglected; the Stage I reaction goes to completion in a few tenths of a second (Table 1), making negligible the possible kinetic effect from the Stage II reaction.

Stage I. The pseudo-first-order rate constant, k_ϕ, for the attainment of an equilibrium (K_1) is the sum of forward and reverse components.[4] For the Stage I reaction the kinetic expression (Eq. 4)

$$k_\phi = k_1([C_2H_5O^-]+[\mathbf{1}]) + k_{-1} \qquad (4)$$

$$k_\phi = k_1[C_2H_5O^-] + k_{-1} \qquad (5)$$

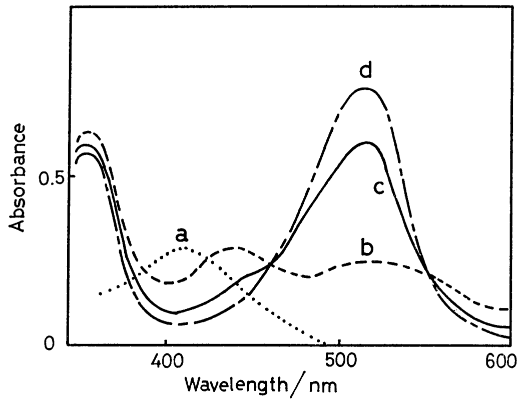


Fig. 1. Spectral change relevant to the reaction of 1-dimethylamino-2,4-dinitronaphthalene (**1**) with C_2H_5OK in DMSO–C_2H_5OH (90:10 v/v) at room temperature.
a: **1** (3.5×10^{-5} M) (1 M=1 mol dm^{-3}), b: just after addition of C_2H_5OK (4.42×10^{-3} M), c: 15 min after addition, d: 90 min after addition.

should hold. Under the actual condition $[C_2H_5O^-]\gg[\mathbf{1}]$, Eq. 4 is simplified to Eq. 5.[5]

As a result, k_1 and k_{-1} are estimated from the slope and intercept in the linear dependence of k_ϕ on $[C_2H_5O^-]$ (not shown). Table 1 shows the dependence of k_ϕ on the ethoxide ion concentration, including the estimated rate and equilibrium constants. Table 2

TABLE 1. RATE AND EQUILIBRIUM CONSTANTS FOR THE FORMATION AND DECOMPOSITION OF 1,3-DISUBSTITUTED ANIONIC σ COMPLEXES FORMED FROM 1-DIMETHYLAMINO-2,4-DINITRONAPHTHALENE (**1**) AND POTASSIUM ALKOXIDES IN (90:10 v/v) AT 25 °C

[ROK] / M	k_ϕ[b)] / s^{-1}	k_1[c)] / $M^{-1}\,s^{-1}$	$10\,k_{-1}$[c)] / s^{-1}	K_1[d)] / M^{-1}
		DMSO-CH_3OH[a)]		
$10^3[CH_3OK]$				
2.16	1.95±0.07			
3.53	2.94±0.09			
6.35	4.66±0.03			
7.20	5.08±0.06			
8.10	5.49±0.10			
8.80	6.05±0.05	607±12[e)]	6.98±1.44[e)]	940± 230[e)]
9.90	6.70±0.06			
11.0	7.37±0.05			
12.0	8.00±0.04			
13.0	8.60±0.07			
14.0	9.27±0.08			
		DMSO-C_2H_5OH[a)]		
$10^3[C_2H_5OK]$				
3.25	3.98±0.05			
4.13	5.11±0.05			
6.50	7.77±0.42			
6.88	8.60±0.07			
9.63	12.0 ±0.1			
9.75	11.6 ±0.1	1190±25	3.00±0.16	4380±1400
12.3	15.2 ±0.7			
15.1	18.5 ±0.1			
16.3	19.5 ±0.5			
17.8	20.0 ±0.7			
19.5	23.0 ±0.8			

a) $[\mathbf{1}]=2.0\times10^{-4}$ M; $\mu=0.05$ ($KClO_4$). b) Measured at 565 nm by the stopped-flow method. c) Calculated from Eq. 5. d) Calculated from $K_1=k_1/k_{-1}$. e) Although the values are a little different from those in Table 1 in Ref. 1, they are more rigorous because of the broader range of $[CH_3OK]$ adopted for the measurement.

Table 2. Temperature dependence of rate constants for the formation and decomposition of 1,3-disubstituted anionic σ complex formed from 1-dimethylamino-2,4-dinitronaphthalene (**1**) and potassium ethoxide in DMSO-C_2H_5OH (90 : 10 v/v)[a)]

Temp °C	k_1 [b)] $M^{-1}\,s^{-1}$	k_{-1} [c)] s^{-1}	K_1 [d)] M^{-1}
15	519± 8	0.10±0.02	5420±1160
25	1190±25	0.30±0.16	4380±1400
35	2430±20	—[e)]	—[e)]
40	3510±60	—[e)]	—[e)]

a) $[\mathbf{1}]_0=2.0\times10^{-4}$ M; $\mu=0.05$ M ($KClO_4$). For the results of the reaction of **1** with CH_3OK, see Table 2 in Ref. 1. b) Calculated from Eq. 5. c) Calculated from Eq. 5. d) Calculated from $K_1=k_1/k_{-1}$. e) Not calculated owing to too large errors.

Table 3. Kinetic and thermodynamic parameters for the formation and decomposition of 1,3-disubstituted anionic σ complexes in DMSO-ROH (90:10 v/v) at 25 °C

	DMSO-CH_3OH[a)]	DMSO-C_2H_5OH
$k_1/M^{-1}\,s^{-1}$	607±12	1190±25
$10\,k_{-1}/s^{-1}$	6.98±1.44	3.00±0.16
K_1/M^{-1}	940±230	4380±1400
ΔH_1^*/kcal mol^{-1}	10.6±2.5	10.8±2.2
ΔS_1^*/e.u.	−10.0±7.4	−8.3±4.5
ΔH_{-1}^*/kcal mol^{-1}	13.4±3.7	—
ΔS_{-1}^*/e.u.	−14.1±11.9	—

a) Cited from Ref. 1.

shows the dependence of k_1, k_{-1}, and K_1 on reaction temperature.

The kinetic and activation parameters obtained from the Arrhenius plot (not shown) are summarized in Table 3.

Stage II. As shown in Fig. 1, the first spectral change (**1**⇄**2a**) can be followed by stopped-flow spectrophotometry, whereas the second one (**2a**⇄**1**⇄**2b**) can be measured by usual spectrophotometry. As a result, the Stage I reaction is very fast compared with the Stage II one, because the time scale of measurement by stopped-flow spectrophotometry is extremely short compared with that by usual spectrophotometry. Therefore, the Stage I reaction can be treated as a fast mobile equilibrium, with shift almost entirely to the right, in treatments of the Stage II kinetics.

As to the rate of the Stage II reaction, the kinetic expression derivable from Eq. 3 should take account of the possibility that the substrate may be split between **1** and **2a**. Putting $[\mathbf{1}]_{st}=[\mathbf{1}]+[\mathbf{2a}]$ and with K_1 standing for the equilibrium constant for the Stage I reaction, one obtains

$$k_{obsd} = k_{-2} + \frac{k_2[C_2H_5O^-]}{1+K_1[C_2H_5O^-]}, \tag{6}$$

where k_{obsd} is the pseudo-first-order rate constant for the Stage II reaction, and k_2 and k_{-2} the rate constants for the forward and reverse reactions.

From Eq. 6, the dependence of k_{obsd} on $[C_2H_5O^-]$ would afford a curvilinear relationship, in which the curve would not pass through the origin. If the k_{-2} value can be obtained by extrapolation from the relationship between k_{obsd} and $[C_2H_5O^-]$, one may derive the following equation by substituting the value into Eq. 6 and rearranging:

$$\frac{1}{k_{obsd}-k_{-2}} = \frac{1}{k_2[C_2H_5O^-]} + \frac{K_1}{k_2}. \tag{7}$$

Thus, k_2 and K_1 can be obtained from the slope and intercept in the plot of $1/(k_{obsd}-k_{-2})$ against $1/[C_2H_5O^-]$. In the inversion plot the k_{-2} value was determined so that the best linear relationship might be established. Therefore, there might be some ambiguity in the k_{-2} values.

Table 4 shows the dependence of k_{obsd} on the alkoxide concentration, including the estimated rate and equilibrium constants. The relationships (Eqs. 6 and 7) hold for the reaction of **1** with CH_3O^- [1)] (Figs. 2 and 3). It is clear, however, that the k_{obsd} values hardly depend upon $[C_2H_5O^-]$.

Discussion

Activation Parameters of Stage I. The difference between the k_1 values depends upon the ΔS_1^* rather than the ΔH_1^* values, although the ΔH_1^* and ΔS_1^* values compensate each other (Table 3). This relationship reasonably arises from the difference between the structures of the transition states leading to **1a** and **2a**. The transition state leading to **2a** would resemble the intermediate **2a** less closely than does the one leading to **1a**; the $C_2H_5O\cdots C_1$ (naphthalene)

Table 4. Rate constant for the formation and decomoosition of 1,1-disubstituted anionic σ complex formed from 1-dimethylamino-2,4-dinitronapthalene (**2**) and potassium ethoxide in DMSO-C_2H_5OH (90:10 v/v) at 25 °C[a)]

$10^3[C_2H_5OK]$ M	$10^3\,k_{obsd}$ s^{-1}	$(k_2/K_1)+k_{-2}$ [b)] s^{-1}
1.00	3.06	
1.22	3.08	
1.30	3.07	
2.00	3.12	
2.44	3.23	
2.61	3.31	
3.00	3.15	
3.66	3.15	
3.91	3.38	$3.18\pm0.16\times10^{-3}$
4.00	3.22	
4.88	3.16	
5.00	3.24	
6.10	3.19	
6.52	3.22	
7.83	3.19	
8.00	3.14	
9.13	3.15	
9.76	3.10	

a) $[\mathbf{2}]_0=3.96\times10^{-5}$ M; $\mu=0.05$ M ($KClO_4$). Measured at λ_{max} 519 nm. For the results of the reaction of **1** with CH_3OK, see Table 4 in Ref. 1. b) The $(k_2/K_1)+k_{-2}$ value is the average of k_{obsd}'s.

bond would be less closer to the covalent bond (C_2H_5O–C_1) in **2a**. This situation would likely originate from the higher nucleophilicity of $C_2H_5O^-$. As a result, the free energy ΔG_1^* ($=\Delta H_1^* - T\Delta S_1^*$) for the forward reaction (Eq. 2a) is less than the free energy ΔG_1^* for the forward reaction (Eq. 1a) due to more delocalization of the negative charge donated by $C_2H_5O^-$.

Stage II. As described previously, the rate expression for Stage II is as shown in Eq. 6. Equation 6 is consistent with the results for the reaction of **1** with CH_3O^- (Fig. 2). The k_{-2} value can be determined by extrapolation of $1/[CH_3O^-]\rightarrow 0$. The inversion plot using the k_{-2} value (Eq. 7) shows a good linearity (Fig. 2).

For the reaction of **1** with $C_2H_5O^-$, however, the k_{obsd} values hardly depend upon $[C_2H_5O^-]$ at the ethoxide ion concentrations studied (Fig. 3). The results could rationally be interpreted as follows: The K_1 value for the reaction of **1** with $C_2H_5O^-$ was determined to be 4380 M^{-1} (1 M=1 mol dm^{-3}). According to this value, $K_1[C_2H_5O^-]$ varies from *ca.* 4 to *ca.* 43 (Table 4). In Eq. 6, then, $1+K_1[C_2H_5O^-]$ is nearly equal to $K_1[C_2H_5O^-]$ except for the $[C_2H_5O^-]$ range 1.00 to 1.30×10^{-3} M. As a result, k_{obsd} is equal to $k_{-2}+(K_2/K_1)$ (Fig. 3). Accordingly, in the case of **1** with $C_2H_5O^-$, too, the reaction will proceed as shown in Eq. 3.

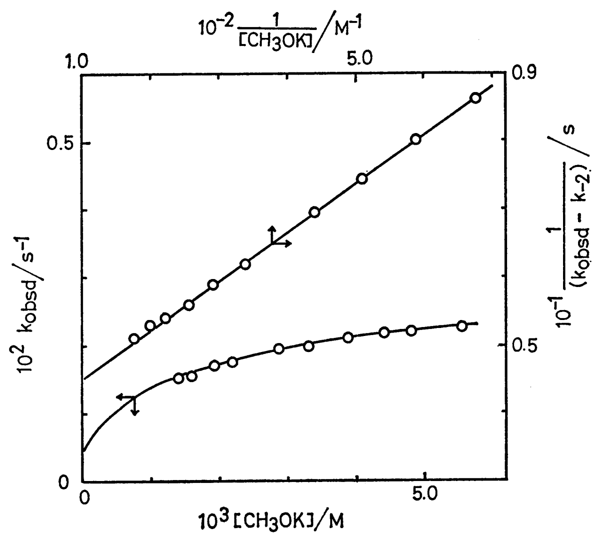


Fig. 2. Relationships between k_{obsd} and $[CH_3OK]$ and between $1/(k_{obsd}-k_{-2})$ and $1/[CH_3OK]$ in naphthalene (**1**) with CH_3OK in DMSO-CH_3OH (90:10 v/v) at 25 °C [cited from Ref. 1]: $[\mathbf{1}]_0$ 3.20×10^{-5} M; μ 0.05 M ($KClO_4$).

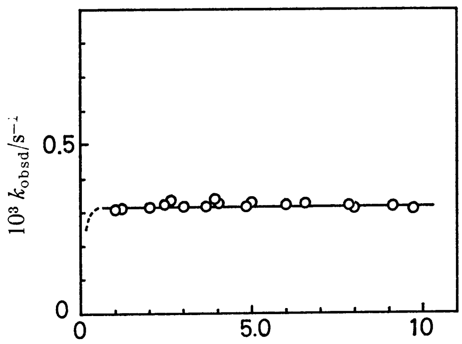
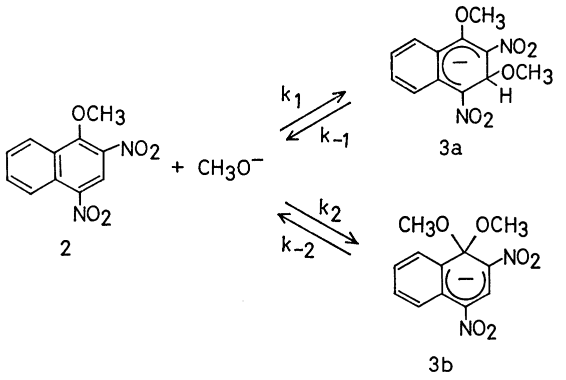


Fig. 3. Relationship between k_{obsd} and $[C_2H_5OK]$ in the reaction of 1-dimethylamino-2,4-dinitronaphthalene (**1**) with C_2H_5OK in DMSO-C_2H_5OH (90:10 v/v) at 25 °C.

It is of interest to compare our results with those of Millot and Terrier,[7] who carried out a kinetic study of the reaction of **2** with potassium methoxide in DMSO-CH_3OH (90:10 v/v) at 20 °C and proposed the sequences



(8a)

(8b)

The values they specified are as follows: k_1 7800 M^{-1} s^{-1}; k_{-1} 8.5 s^{-1}; K_1 916 M^{-1}; k_2 2100 $M^{-1}\,s^{-1}$; k_{-2} too small to be decided.

With the Stage I reactions (Eqs. 1a, 2a, and 8a), the k_1 and k_{-1} values for the reaction of **2** with CH_3O^- are the largest, but the K_1 values are similar in both cases (Eqs. 1a and 8a), whereas the K_1 value for the reaction of **1** with $C_2H_5O^-$ (Eq. 2a) is much larger than those in the other cases (Eqs. 1a and 8a). Further, the $k_1(\mathbf{3a})/k_1(\mathbf{1a})$ and $k_{-1}(\mathbf{3a})/k^{-}_{1}(\mathbf{1a})$ ratios are *ca.* 12, whereas the $k_1(\mathbf{3a})/k_1(\mathbf{2a})$ and $k_{-1}(\mathbf{3a})/k_{-1}(\mathbf{2a})$ ratios are *ca.* 6.6 and *ca.* 28, respectively. That is to say, in the former cases (Eqs. 1a and 8a) the k_1 and k_{-1} ratios are quite the same, whereas in the latter (Eq. 2a) the k_1 ratio is about one seventh the k_{-1} ratio. The difference arises from the fact that the free energy (ΔG_1^*) for the reaction of **1** with $C_2H_5O^-$ is the least among the three cases (Eqs. 1a, 2a, and 8a) and, then, the complex **2a** is the most stable as described above.

In conclusion, it is confirmed that the reactions of 1-dialkylamino-2,4-dinitronaphthalenes with alkoxides will proceed according to Eq. 1 and that the larger the nucleophilicity of alkoxides is, the stabler are the anionic σ complexes.[7]

Experimental

NMR spectra were recorded on a Varian A-60D spectrometer and UV-VIS absorption spectra on a Hitachi Model 200-10 spectrophotometer.

Materials. Compound **1** was prepared according to the method described previously.[7] A small amount of calcium hydride was added to commercial dimethyl sulfoxide, which was then distilled under reduced pressure prior to use. Commercial potassium perchlorate of special grade was used without further purification, *Rate Measurement.* As regards the kinetics of formation and decomposition of 1,3-disubstituted anionic σ complex, the transmittance of the complex was measured in order to estimate the apparent pseudo-first-order rate constants (k_{ϕ}) with a thermostated Union RA-1300 Stopped-Flow Analyser (Union Giken). The kinetic measurements for the formation and decomposition of 1,1-disubstituted ones (k_{obsd}) were made with a thermostated Hitachi Model 200-10 Spectrophotometer.

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4) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York (1965), p. 19.

5) Strictly speaking, $[C_2H_5O^-]_e$ and $[\mathbf{2}]_e$ (the suffix e represents the concentration at the attainment of equilibrium) should be substituted for $[C_2H_5O^-]$ and $[\mathbf{2}]$.[4)]

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