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Aromatic Nucleophilic Substitution. XV.[1] Stopped-flow Kinetics of the Formation and Decomposition of 1,3- and 1,1-Disubstituted Meisenheimer Complexes in the Reactions of 1-Dialkylamino-2,4-dinitronaphthalenes with Potassium Methoxide in Dimethyl Sulfoxide-Methanol

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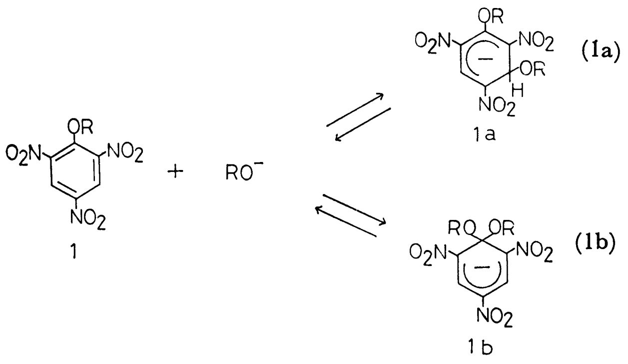
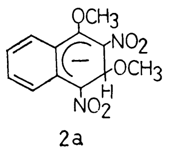
The formation of 1,3-disubstituted anionic σ complexes, followed by 1,1-disubstituted ones was confirmed by means of absorption and NMR spectra in the reactions of 1-dialkylamino-2,4-dinitronaphthalenes with potassium methoxide in DMSO–CH_3OH. The rates and activation parameters were determined by kinetic studies with use of stopped-flow and conventional spectrophotometers. The rate constants for the formation of 1,3-disubstituted one decreased in the order 1-dimethylamino- > 1-(*N*-methylbutyl)amino- > 1-piperidino- > 1-diethylamino-2,4-dinitronaphthalenes, those for its decomposition being comparable with each other. On the other hand, the rate constant for the formation of 1,1-disubstituted one decreased in the same order as above while that for its decomposition decreased in the order 1-dimethylamino- > 1-(*N*-methylbutyl)amino- > 1-diethylamino- > 1-piperidino-2,4-dinitronaphthalenes. The mechanism was discussed from activation parameters.

Many Jackson-Meisenheimer complexes (anionic σ complex) have been prepared by nucleophilic attack on polynitroaromatic compounds[2] as shown by



Especially in the reactions of 1-alkoxy- or 1-amino-substituted activated benzenes or heteroaromatics with alkoxides or amines, two anionic σ complexes, 1,3- and 1,1-disubstituted ones (**1a** and **1b**) are usually formed.[3–22] Upon addition of bases **1a** is formed at first, undergoing isomerization to **1b**; the former is said to be a kinetically controlled product and the latter an equilibrium-controlled one.[23,24]

However, with activated naphthalene derivatives 1,3-disubstituted complexes such as **1a** have hardly been found. As a few exceptional cases, Millot and Terrier testified the formation of **2a** by stopped-flow spectrophotometric technique,[14] although its evidence was considered to be somewhat uncertain. Fendler *et al.*[25] attempted the reaction of 1-methoxy-2,4-dinitronaphthalene (**2**) with alkoxide, but were unsuccessful in the identification of **2a**. Their failure is due to the insufficient stability of such complexes as **2a**, as compared with those formed from benzene derivatives.



2a

Thus, if the stability of **2b** (naphthalene analog corresponding to **1b**) could be reduced, the energy barrier between **2a** and **2b** would become smaller, elongating the life of **2a** and making the identification easier. Such attempts were successful in the reactions of 1-amino-2,4-dinitronaphthalenes with alkoxides.[26,27] Replacement of amino for alkoxyl groups clearly deactivates the C-1 position of a naphthalene moiety, necessitating the slower isomerization of **2a** to **2b**.

As a result, it would be interesting to investigate the kinetic and thermodynamic parameters of the reactions of 1-dialkylamino-2,4-dinitronaphthalenes with alkoxides.[28]

This paper reports the stopped-flow kinetics of the formation and decomposition of the 1,3- and 1,1-disubstituted anionic σ complexes in the reactions of various 1-dialkylamino-2,4-dinitronaphthalenes (**3**—**6**) with potassium methoxide in DMSO–CH_3OH (90/10 v/v).

Results

General Features. The reaction of 1-dimethylamino-2,4-dinitronaphthalene (**4**) with potassium methoxide in DMSO–CH_3OH afforded **4a** at first and then **4b** in quantitative yields (Fig. 1). Spectrum (b) obtained by stopped-flow spectrophotometry just after addition of methoxide is due to **4a**, absorbance scale being arbitrary; Spectrum (c), attributable to **4b**, was obtained in 12 min after addition.[29,30] From the results, the reaction is expected to proceed in a mode similar to that of Eq. 1.

NMR technique is considered useful for elucidating the structures of anionic σ complexes.[23] Just after addition of methanolic potassium methoxide (1.40×10^{-4} mol) to a DMSO solution (0.5 ml) of **4** (1.40×10^{-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 8.63) of **4** shifted upfield

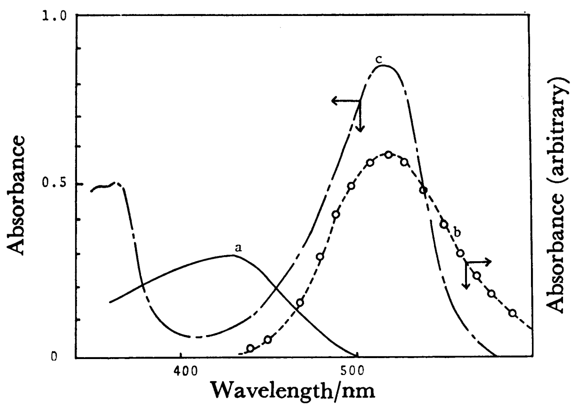
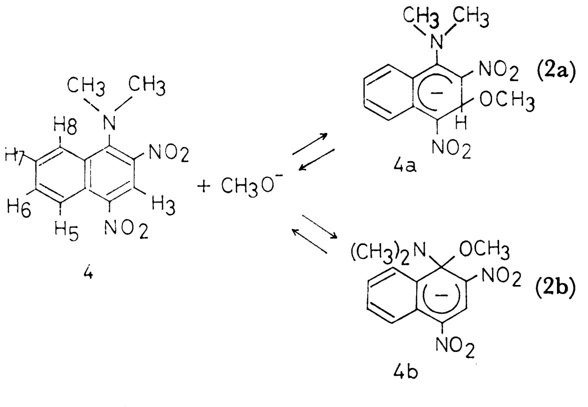


Fig. 1. Spectral changes relevant to the reaction of 1-dimethylamino-2,4-dinitronaphthalene (**4**) with CH_3OK in DMSO–CH_3OH (90 : 10, v/v); (a) **4** (3.25×10^{-5} M (1M=1 mol dm^{-3}) at room temperature; (b) obtained by means of a stopped-flow method (**4** 5.0×10^{-4} M and CH_3OK 4.5×10^{-3} M); (c) 12 min after addition of CH_3OK.



(δ 6.33, H_3 of **4a**). Fast sweep time (500 Hz/50 s) and fast procedure are indispensable for detecting spectral changes, 2.5 min after addition, a new singlet, due to H_3 of **4b** appeared at δ 9.31 at the expense of the singlet at δ 6.33 (measured at the normal sweep time, 250 Hz/50 s, in this case) which appeared faintly.

The results also support the reaction paths (Eq. 2). Similar results were obtained for **3**, **5**, and **6**.[31] It is thus expected that the discrete kinetics of formation and decomposition of **4a** and **4b** is possible.

Kinetic Runs. Let us rewrite Eq. 2 in a form convenient for quantitative discussion as Eq. 3. Stage I kinetics (**4**⇄**4a**, Eq. 3a) is much faster than Stage II

$$\begin{tikzcd} & \mathbf{4a}\ \text{(3a)} \arrow[dl, shift left, "k_{-1}"] \\ \mathbf{4} + {}^{-}\mathrm{OCH_3} \arrow[ur, shift left, "{k_1, K_1}"] \arrow[dr, shift left, "{k_2, K_2}"] & \\ & \mathbf{4b}\ \text{(3b)} \arrow[ul, shift left, "k_{-2}"] \end{tikzcd} \qquad K_1 = \frac{k_1}{k_{-1}},\ K_2 = \frac{k_2}{k_{-2}}$$

reaction (**4**⇄**4b**, Eq. 3b). Thus, when Stage I kinetics is taken into account, Stage II reaction can be neglected, since the former reaction is completed in several thousandths seconds (Table 3), making the contamination by the latter negligible.

Stage I. The pseudo-first-order rate constant, k_ϕ, for the attainment of an equilibrium is the sum of forward and reverse components. For the system (Eq. 3a) the following expression should hold:

$$k_\phi = k_1([\mathrm{CH_3O^-}]+[\mathbf{4}]) + k_{-1}. \tag{4}$$

Under the usual condition $[\mathrm{CH_3O^-}] \gg [\mathbf{4}]$, Eq. 4 is simplified to

$$k_\phi = k_1[\mathrm{CH_3O^-}] + k_{-1}. \tag{5}$$

As a result, dependence of k_ϕ on methoxide concentration would afford the linear relationship, and k_1 and k_{-1} are estimated from the slope and the intercept, respectively. The dependence of k_ϕ on methoxide concentration is given in Table 1, involving estimated rate constants and equilibrium constants. The relationship between k_ϕ and methoxide concentration at 15, 25, and 35 °C indicates that Eq. 5 holds fairly well (Fig. 2). The temperature dependence of K_1, k_1, and k_{-1} was determined at four temperatures. Kinetic and activation parameters obtained from the Arrhenius plot (not shown) are summarized in Table 3, which includes the results obtained for **3**, **5**, and **6**. The k_1 values decrease in the order **4**>**5**>**3**>**6** and the k_{-1} values in the order **3**>**6**>**4**>**5**. The enthalpy and entropy of activation for **3**, **4**, **5**, and **6** ($\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$) compensate with each other, and those ($\Delta H_{-1}^{\ddagger}$ and $\Delta S_{-1}^{\ddagger}$) also do the same except for **3**, in which the k_{-1} value depends upon $\Delta S_{-1}^{\ddagger}$ rather than $\Delta H_{-1}^{\ddagger}$.

Stage II. As shown in Fig. 1, the change from Spectrum a to Spectrum b (**4**⇄**4a**) obtained by stopped-flow spectrophotometry is instantaneous, whereas that from Spectrum b to Spectrum c (Stage II reaction) is relatively slow. As a result, Stage II reaction (**4a**⇄**4**⇄**4b**), in which Stage I process (**4**⇄**4a**) is involved as equilibrium, is much slower than Stage I reaction. Therefore, Stage I reaction can be treated as equilibrium, lying almost entirely on the right in the treatment of Stage II kinetics. Table 3 shows that Stage I reaction

Table 1. Rate and equilibrium for the formation and decomposition of 1,3-disubstituted anionic σ complex formed from 1-dimethylamino-2,4-dinitronaphthalene (**4**) and potassium methoxide in DMSO–CH_3OH (90: 10 v/v) at 25 °C[a)]

10^3 [CH_3OK] / M	k_ϕ[b)] / s^{-1}	k_1 / $M^{-1}\,s^{-1}$	$10\,k_{-1}$ / s^{-1}	K_1 / M^{-1}
2.16	1.95			
2.26	2.11			
3.53	2.94			
4.24	3.19			
4.50	3.38			
4.94	3.63	596[c)]	7.24[d)]	820[e)]
5.40	3.92			
5.65	4.04			
6.35	4.66			
7.20	5.08			
8.10	5.49			

a) $[\mathbf{4}]_0$ 2.0×10^{-4} M; μ 0.05 M ($KClO_4$). b) Measured at 565 nm with a stopped-flow method. Estimated limit of error ±2.5%. c) Calculated from Eq. 5. Estimated limit of error ±7.3%. d) Calculated from Eq. 5. Estimated limit of error ±10.0%. e) Calculated from $K_1 = k_1/k_{-1}$.

TABLE 2. TEMPERATURE DEPENDENCE OF k_1, k_{-1}, AND K_1 FOR THEFORMATION AND DECOMPOSITION OF 1,3-DISUBSTITUTED ANIONIC σ COMPLEX FORMED FROM 1-DIMETHYLAMINO-2, 4-DINITRONAPHTHALENE (**4**) AND POTASSIUM METHOXIDE IN DMSO-CH_3OH (90: 10 v/v)[a]

Temp °C	k_1[b] $M^{-1}\,s^{-1}$	$10\,k_{-1}$[c] s^{-1}	K_1[d] M^{-1}
15	325	2.83	1150
25	596	7.24	820
35	1150	14.8	780
40	1570	20.2	710

a) $[4]_0$ 2.0×10^{-4} M; μ 0.05 M ($KClO_4$). b) Calculated from Eq. 5. Estimated limit of error ±7.3%. c) Calculate from Eq. 5. Estimated limit of error ±10.0%. d) Calculated from $K_1=k_1/k_{-1}$. Estimated limit of error ±17.3%.

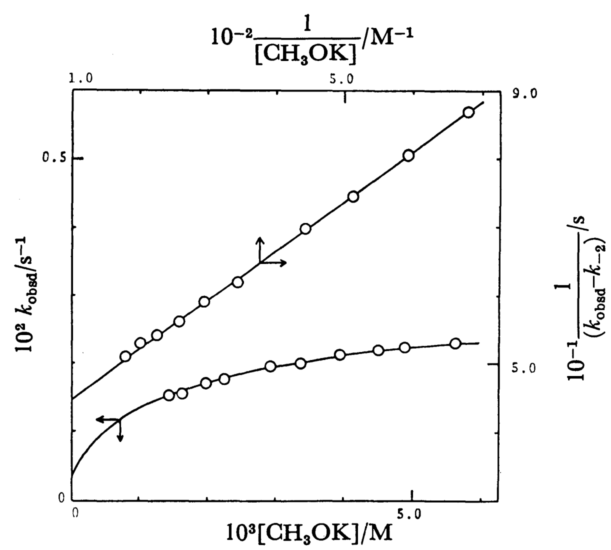


Fig. 2. Relationship between k_{obsd} and $[CH_3OK]$ and between $1/(k_{obsd}-k_{-2})$ and $1/[CH_3OK]$ in the reaction of 1-dimethylamino-2,4-dinitronaphthalene with CH_3OK in DMSO-CH_3OH (90 : 10, v/v) at 25 °C.

nearly completed in several thousandths of a second, very small in the time scale for Stage II reaction.

As to the rate of Stage II reaction, the general kinetic expression derivable from Eq. 3 should take account of the possibility that the substrate may be split between **4** and **4a**. Putting $[\mathbf{4}]_{st}=[\mathbf{4}]+[\mathbf{4a}]$, and K_1 the equilibrium constant for Stage I reaction, we obtain

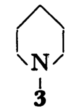
$$k_{obsd}=k_{-2}+\frac{k_2[CH_3O^-]}{1+K_1[CH_3O^-]}, \tag{6}$$

where k_{obsd} is the pseudo-first-order rate coefficient for Stage II reaction, and k_2 and k_{-2} the rate coefficients for forward and reverse reactions. Consequently, dependence of k_{obsd} on methoxide concentration 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 methoxide concentration, we obtain the following equation by substituting the value into Eq. 6, and rearranging. Thus, k_2 and k_1 can be obtained from the slope and intercept in the plot of $1/(k_{obsd}-k_{-2})$ against $1/[CH_3O^-]$.

$$\frac{1}{k_{obsd}-k_{-2}}=\frac{1}{k_2[CH_3O^-]}+\frac{K_1}{k_2} \tag{7}$$

The dependence of k_{obsd} on methoxide concentration involves estimated rate and equilibrium constants (Table 4). Figure 2 shows the dependence of k_{obsd} on methoxide concentration and the inversion plot. Equation 6 and 7 are seen to hold. Objection might arise that the relation between k_{obsd} and methoxide concentration (Fig. 2) would afford a straight line within the range of methoxide concentration. This would be expected if $K_1[CH_3O^-]\ll1$ in Eq. 6. Although an increase in k_{obsd} with increasing methoxide concentration is much smaller at 25 °C, the plot of k_{obsd} against methoxide concentration were steeply convex upward at higher temperatures (*e.g.*, 35 and 40 °C), indicating that Eq. 6 holds. The k_{-2} value was so determined that the best linear relationship would be established in the inversion plot (Eq. 7). There might be some

TABLE 3. KINETIC AND THERMODYNAMIC PARAMETERS FOR THE FORMATION AND DECOMPOSITION OF 1,3-DISUBSTITUTED ANIONIC σ COMPLEXES IN DMSO–CH_3OH (90: 10 v/v) AT 25 °C

R R'[a] N	 **3**	CH_3 CH_3 N **4**	CH_3 n-C_4H_9 N **5**	C_2H_5 C_2H_5 N **6**
$k_1/M^{-1}\,s^{-1}$	480±35	596±44	540±40	410±30
k_{-1}/s_{-1}	1.04±0.11	$7.24\pm0.08\times10^{-1}$	$7.20\pm0.08\times10^{-1}$	$7.56\pm0.08\times10^{-1}$
K_1/M^{-1}	460±80	820±150	750±140	540±90
$\Delta H_1^{\ddagger}$/kcal mol^{-1}	11.5±2.3	10.6±2.2	11.2±2.3	12.1±2.5
$\Delta S_{-1}^{\ddagger}$/cal deg^{-1} mol^{-1}	−7.1±5.3	−10.0±7.6	−8.1±6.5	−5.7±4.3
$\Delta H_{-1}^{\ddagger}$/kcal mol^{-1}	13.5±3.6	13.4±3.6	13.7±3.6	14.1±3.7
$\Delta S_{-1}^{\ddagger}$/cal deg^{-1} mol^{-1}	−10.9±9.2	−14.1±12.0	−12.9±10.9	−11.4±9.7
$\Delta H_{1,3}^{\circ}$/kcal mol^{-1} [b]	−2.0±5.9	−2.8±5.8	−2.5±5.9	−2.0±6.2
$\Delta S_{1,3}^{\circ}$/cal deg^{-1} mol^{-1} [c]	3.8±14.5	4.1±19.6	4.8±17.4	5.7±14.0
$\Delta G_{1,3}^{\circ}$/kcal mol^{-1} [d]	−3.1±10.2	−4.0±11.6	−3.9±11.2	−3.7±10.3

a) Only the substituent at C-1 of 2,4-dinitronaphthalene is indicated. b) $\Delta H_{1,3}^{\circ}=\Delta H_1^{\ddagger}-H_{-1}^{\ddagger}$. c) $\Delta S_{1,3}^{\circ}=S_1^{\ddagger}-S_{-1}^{\ddagger}$. d) $\Delta G_{1,3}^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$.

TABLE 4. RATE AND EQUILIBRIUM FOR THE FORMATION AND DECOMPOSITION OF 1,1-DISUBSTITUTED ANIONIC σ COMPLEX FORMED FROM 1-DIMETHYLAMINO-2,4-DINITRONAPHTHALENE (**4**) AND POTASSIUM METHOXIDE IN DMSO–CH_3OH(90: 10 v/v) AT 25 °C[a)]

$10^3\,[CH_3OK]$ M	$10^2\,k_{obsd}$[b)] s^{-1}	k_2 $M^{-1}\,s^{-1}$	$10^3\,k_{-2}$ s^{-1}	K_1 M^{-1}	K_2 M^{-1}
1.47	1.51	14.3[c)]	3.6[d)]	540[e)]	3970[f)]
1.69	1.60				
1.96	1.70				
2.25	1.76				
2.93	1.97				
3.37	2.05				
3.91	2.13				
4.49	2.20				
4.89	2.25				
5.62	2.31				

a) $[\mathbf{4}]_0$ 3.20×10^{-5} M; μ 0.05 M ($KClO_4$). b) Measured at 520 nm. Estimated limit of error ±2.0%. c) Calculated from Eq. 7. Estimated limit of error ±13.5%. d) Calculated from Eq. 6. Estimated limit of error ±8.3%. e) Estimated limit of error ±16.5%. f) Calculated from $K_2=k_2/k_{-2}$. Estimated limit of error ±21.7%.

TABLE 5. TEMPERATURE DEPENDENCE OF K_1, K_2, k_2, AND k_{-2} FOR FORMATION AND DECOMPOSITION OF THE 1,1-DISUBSTITUTED ANIONIC σ COMPLEX FORMED FROM 1-DIMETHYLAMINO-2,4-DINITRONAPHTHALENE (**4**) AND POTASSIUM METHOXIDE IN DMSO–CH_3OH (90: 10 v/v) AT 25 C°[a)]

Temp °C	k_2[b)] $M^{-1}\,s^{-1}$	$10^3\,k_{-2}$[c)] s^{-1}	K_1[d)] M^{-1}	K_2[e)] M^{-2}
15	6.7	2.5	680	2680
25	14.3	3.6	540	3970
35	28.5	5.1	440	5580
40	41.8	5.8	400	7200

a) $[\mathbf{4}]_0$ 3.20×10^{-5} M; μ 0.05 M ($KClO_4$). b) Estimated limit of error ±13.5%. c) Estimated limit of error ±8.3%. d) Estimated limit of error ±16.5%. e) Estimated limit of error 21.7%.

ambiguity in the k_{-2} values. The temperature dependence of K_1, K_2, k_2, and k_{-2} at four temperatures is given in Table 5. The Arrhenius plot affords kinetic and activation parameters (Table 6), together with the results obtained for **3**, **5**, and **6**. Although there is some difference between the K_1 values obtained from Stage I and II kinetics, the agreement could be considered to be fairly good. Formation of 1,3-disubstituted anionic σ complex is kinetically controlled and that of 1,1-disubstituted one equilibrium-controlled, which is reflected in the K_1 and K_2 values (Tables 3 and 6).

Discussion

1,3-Disubstituted Anionic σ Complex. The rates and activation parameters (Table 3) do not differ much, since methoxide ion attacking at the C-3 position does not get the direct effect of a dialkylamino group at the C-1 position. Some comments are given in the following. (a) The entropy of activation for k_{-1} is negative, as compared with that for k_1 with each substrate. This indicates that the entropy refers to unimolecular reactions in line with the view that part of the negative charge delocalized in the anionic σ complex becomes concentrated on the incipient methoxide ion in the transition state of decomposition, increasing the solvation of activated complexes and giving rise to negative entropy of activation.[33)] (b) The enthalpy and entropy of activation for k_1 ($\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$) compensate each other, in line with the view that the solvation of methanol to the dialkylamino group of a substrate, in which the F- and B-strains proposed by Brown *et al.*[34–36)] occur,

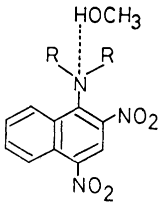
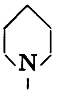


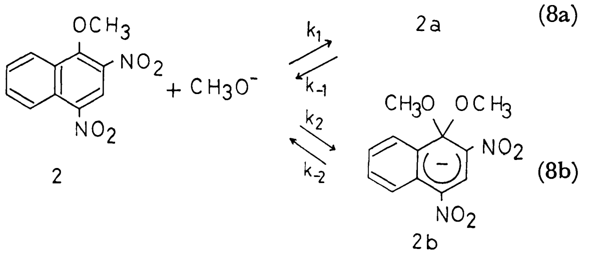
TABLE 6. KINETIC AND THERMODYNAMIC PARAMETERS FOR THE FORMATION AND DECOMPOSITION OF 1,1-DISUBSTITUTED ANIONIC σ COMPLEXES IN DMSO–CH_3OH (90: 10 v/v) AT 25 °C

R R′[a)] N	 **3**	CH_3 CH_3 N **4**	CH_3 $n\text{-}C_4H_9$ N **5**	C_2H_5 C_2H_5 N **6**
$k_2/M^{-1}\,s^{-1}$	2.53 ± 0.29	14.3 ± 1.9	3.88 ± 0.38	1.09 ± 0.14
k_{-2}/s^{-1}	$1.8\pm1.3\times10^{-4}$	$3.6\pm0.3\times10^{-4}$	$1.2\pm0.1\times10^{-4}$	$3.3\pm0.3\times10^{-4}$
K_1/M^{-1}	310 ± 50	540 ± 90	350 ± 60	290 ± 50
K_2/M^{-1}	14100 ± 3050	3970 ± 860	2400 ± 520	2200 ± 710
$\Delta H_2^{\ddagger}$/kcal mol^{-1}	12.2 ± 2.5	12.1 ± 2.5	13.1 ± 2.7	14.4 ± 3.0
$\Delta S_2^{\ddagger}$/cal deg^{-1} mol^{-1}	-15.4 ± 10.2	-12.8 ± 8.5	-12.3 ± 8.1	-11.9 ± 7.9
$\Delta H_2^{\ddagger}$/kcal mol^{-1}	27.2 ± 7.2	5.3 ± 1.4	11.4 ± 3.0	8.2 ± 2.1
$\Delta S_2^{\ddagger}$/cal deg^{-1} mol^{-1}	-15.8 ± 1.5	-51.9 ± 4.9	-33.3 ± 3.1	-48.7 ± 4.6
$\Delta H^0_{1.1}$/kcal mol^{-1}	-15.0 ± 9.7	6.8 ± 3.9	1.7 ± 5.7	6.2 ± 5.1
$\Delta S^0_{1.1}$/cal deg^{-1} mol^{-1}	0.4 ± 11.7	39.1 ± 13.4	21.0 ± 11.2	36.8 ± 12.5
$\Delta G^0_{1.1}$/kcal mol^{-1}	-15.1 ± 12.2	-4.8 ± 4.9	-4.6 ± 9.0	-4.8 ± 8.8

a) Only the substituent at C-1 of 2,4-dinitronaphthalene is indicated. b) $\Delta H^0_{1.1}=\Delta H_2^{\ddagger}-\Delta H^{\ddagger}_{-2}$. c) $\Delta H^0_{1.1}=\Delta H_2^{\ddagger}-\Delta H^{\ddagger}_{-2}$. d) $\Delta G^0_{1.1}=\Delta H^0_{1.1}-T\Delta S^0_{1.1}$.

would make amino nitrogen ammonium-nitrogen-like, which exerts the less electron-donating resonance contribution (due to the lone pair electrons of the amino nitrogen), giving rise to the reduced deactivation of the C-3 position indirectly. Naturally, the bulkier an amino group, the less it is solvated by methanol. Thus, the compensation would be evolved between the enthalpy and entropy of activation ($\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$). As regards the enthalpy and entropy of activation for k_{-1} ($\Delta H^{\neq}_{-1}$ and $\Delta S^{\neq}_{-1}$), those on **4**, **5**, and **6** linearly compensate each other except for **3**. With **3**, the compensation between $\Delta H^{\neq}_{-1}$ and $\Delta S^{\neq}_{-1}$ was found to deviate somewhat from the linear relationship. The conformation of **3** could be taken into account. In veiw of solvation ($-NR_2 \cdots HOCH_3$), the 2,5-dinitro-1-naphthyl group should be put into an equatorial position at the nitrogen atom of piperidine. The same conformation could be held also in the anionic σ complex (**3a**). In the unimolecular decomposition of **3a**, the less solvation of methanol to the incipient methoxide ion at the C-3 position would be respon sible for the deviation to some extent, because 1-methoxy-2,6-dinitro-4,5-benzo-3-cyclohexadienylido group is very large.

It is of interest to compare our results with those of Millot and Terrier,[11] who carried out the kinetics of the reaction of **2** with potassium methoxide in DMSO–CH_3OH (90 : 10, v/v) at 20 °C, although their identification of the 1,3-disubstituted anionic σ complex was somewhat imcomplete (Eq. 8). Their values are as follows: k_1 7800 $M^{-1} s^{-1}$; k_{-1} 8.5 s^{-1}; K_1 916 M^{-1}.



Their reaction temperature is a little lower than ours, but the k_1 and k_{-1} values are considerably larger; the difference in the K_1 values is not large. The stronger inductive (−I) and weaker resonance (+R) effects, that is, the more electron-attracting effect of methoxyl group than those of dialkylamino group, activate the C-3 position more strongly, making the attack of methoxide ion faster (k_1). The effects of methoxyl group activate the C-1 position also more strongly, making the 3→1 migration of methoxyl group easier (k_{-1}).

1,1-Disubstituted Anionic σ Complex. The k_2 and k_{-2} values are expected to vary with the steric and activating effects of a substituent at the C-1 position (Table 6). The k_2 value increases in the order **6**<**5**<**4**, depending on the enthalpy of activation ($\Delta H_2^{\neq}$) rather than on the entropy of activation ($\Delta S_2^{\neq}$), in which the same effect ($-NR_2 \cdots HOCH_3$) might function. However, in the case of **3**, the decrease in the k_2 value, seems to depend on the negative and large entropy of activation, which might occur from the steric interference of piperidyl group with the bimolecular attack of methoxide ion at the C-1 position.

Non-linear compensation takes place among the enthalpy and entropy of activation for the decomposition of complex. Especially in the case of **3**, the k_{-2} value depends on the enthalpy of activation rather than on the entropy of activation. The steric strain at the C-1 position of **3**, due to the bulkiness of piperidyl group would be relieved during the formation of complex. This might make the complex more stable, making the k_{-2} value smaller.

Millot and Terrier[11] reported the following constants for the formation and decomposition of 1,1-disubstituted anionic σ complex (Eq. 8b): k_2 2100 $M^{-1} s^{-1}$; k_{-2} too small to be decided.

In the case of **2**, the k_{-2} value is very small, and the K_2 value might be very large. The conpicuous constrast is the difference in the k_2 values, which indicates the steric and inductive advantageousness of methoxyl group. The k_1/k_2 ratios are *ca.* 40—380 in our case, whereas it is *ca.* 4 in the case of Millot and Terrier, which also represents the advantageousness.

In the reaction course of 1-dialkylamino-2,4-dinitronaphthalenes with potassium methoxide in DMSO–CH_3OH, the existance of 1,1- and 1,3-disubstituted anionic σ complexes was confirmed, the life of the latter being much shorter.

Experimental

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

Materials. The compounds (**3**, **4**, **5**, and **6**) were prepared according to the method described previously.[38] A small amount of calcium hydride was added to commercial dimethyl sulfoxide, which was then distilled under reduced pressure. Methanol was refluxed with magnesium for 1 h and distilled. 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 complex was measured in order to estimate the apparent rate constants(k_ϕ) with a thermostatted stopped-flow spectrophotometer (Union RA-1300 Stopped-Flow Analyser). The kinetic measurements for the formation and decomposition of 1,1-disubstituted ones (k_{obsd}) were made with a thermostatted Hitachi Model 200-10 Spectrophotometer.

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