J. Org. Chem. **1984**, *49*, 93–96

tween the effects on the two steps may be related to the fact that the latter reaction accompanies the hybridization changes (sp^2 to sp^3) of the 2-carbon involved in the dithiane ring, but the former does not undergo such a change. The 2-carbon is sp^2 hybridized in both states of 1 and 2 and so are the two adjacent sulfur atoms. However, these three atoms become sp^3 hybridized in 3. As a result, the forced planarity involving the S–C–S triad induces a considerable strain to the dithiane ring of 1 and 2, but such a strain does not occur in 3. The strain does not change during the first step, but it is largely relieved during the second step of the hydrolysis of 1. This would make the hydration of 2 faster than that of the acyclic analogue.

Experimental Section

Materials. 2-Methylene- (**1a**), 2-ethylidene- (**1b**), and 2-benzylidene-1,3-dithiane (**1c**) were prepared from 2-lithio-2-(trimethylsilyl)-1,3-dithiane and an appropriate aldehyde by the method of Seebach.[31] Boiling points were as follows: **1a**, 105 °C (22 mmHg) [lit.[31] 100 °C (20 mmHg)]; **1b**, 83 °C (2.5 mmHg) [lit.[31] 83 °C (2.5 mmHg)]; **1c**, 133–135 °C (0.1 mmHg) [lit.[31] 148 °C (0.2 mmHg)]. Other materials were obtained as described previously.[2]

Kinetic Measurements. Rate constants were determined in the same way as before.[2] Reactions at low acidities were carried out in aqueous HCl and buffer solutions containing 10 vol % of acetanitrile at 30 °C, the ionic strength being maintained at 0.45 M with KCl. Wholly aqueous $HClO_4$ solutions were used without any added salt for the reactions at higher acidities. Acid concentrations were determined by titration with a standard NaOH solution. Reactions were followed spectrophotometrically at an appropriate wavelength on a Shimadzu UV 200 spectrophotometer. The pH values of 10% $CH_3CN–H_2O$ solutions were measured on a Hitachi-Horiba F-7 pH meter and corrected by subtracting 0.06 from the pH meter readings.[2]

Registry No. 1a, 21777-31-1; **1b**, 51102-62-6; **1c**, 17590-58-8; deuterium, 7782-39-0; 2-mercaptoethanol, 60-24-2.

Supplementary Material Available: Tables S1 and S2 consisting of rate constants for the hydrolysis of 1 in buffer solutions and in the presence of 2-mercaptoethanol (2 pages). Ordering information is given on any current masthead page.

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Aromatic Nucleophilic Substitution. 19.[1] Kinetics of the Formation and Decomposition of 1,1-Disubstituted Naphthalene Meisenheimer Complexes in the Reactions of 1-Methoxy-2-cyano-4-nitronaphthalene with Various Metal Methoxides in Methanol. Evidence for Absence of Ion Pairing of Meisenheimer Complexes with Counterions

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The reactions of 1-methoxy-2-cyano-4-nitronaphthalene (2) with various metal methoxides have been studied. In the reactions of 2 with sodium, potassium, and lithium methoxides there are no minima in the relationships between k_ψ (pseudo-first-order rate constant) and alkoxide concentrations, which shows the absence of ion pairing of an anionic σ complex with a counterion. Furthermore, the K_c value (apparent equilibrium constant) increases slightly with increasing alkoxide concentration. Replacement of a cyano group at C-2 destabilized 2^- (1,1-dimethoxy-substituted anionic σ complex of 2) in comparison with 1^- [1,1-dimethoxy-substituted anionic σ complex of 1-methoxy-2-nitro-4-cyanonaphthalene (1)].

Anionic σ complexes (Meisenheimer complexes) have been synthesized by attack of nucleophiles on polynitro aromatic compounds.[2] Furthermore, much evidence has accumulated for many nucleophilic aromatic substitution reactions that involve such complexes as intermediates.[3] Accordingly, much attention is concentrated on the stabilities and rates of formation and decomposition of such complexes. Naphthalene anionic σ complexes have been investigated in the reactions of several nitronaphthalenes with metal alkoxides.[2,4-10]

We previously reported the kinetics of formation and decomposition of the 1,1-disubstituted naphthalene anionic σ complexes (hereafter called complexes) in the reactions of 1-methoxy-2-nitro-4-cyanonaphthalene (1) with metal alkoxides in methanol, in which ion pairing took place between a complex and a counterion (Na^+ or K^+), as a result of the 2-nitro group in some cases.[3] In order to make sure of these results, we have carried out the reactions of 1-methoxy-2-cyano-4-nitronaphthalene (2) with three

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† University of Miyazaki.

(1) Part 18: Sekiguchi, S.; Hirai, M.; Tomoto, N. *Bull. Chem. Soc. Jpn.*, in press.

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Table I. Rate and Equilibrium Data for the Formation of the Anionic σ Complex from 1-Methoxy-2-nitro-4-cyanonaphthalene (2) and Sodium Methoxide in Methanol at 25 °C

10^2[CH$_3$ONa], M	OD,[b] 407 nm	K_c,[c] M^{-1}	10^2k_ψ,[d] s^{-1}	k_1,[e] M^{-1} s^{-1}	10^2k_{-1},[f] s^{-1}
		Part A[a]			
0.96	0.133	2.97	6.80	0.196	6.60
1.50	0.192	3.16	6.86	0.201	6.36
2.40	0.279	3.20	7.14	0.212	6.63
3.61	0.395	3.28	7.29	0.214	6.52
4.51[g]	0.105	3.60	7.18	0.222	6.17
6.01[g]	0.135	3.71	7.63	0.231	6.23
7.52[g]	0.144	3.22	7.48	0.194	6.02
8.42[g]	0.158	3.26	7.98	0.204	6.26
9.62[g]	0.178	3.36	8.01	0.203	6.04
10.5[g]	0.190	3.38	8.27	0.206	6.09
		av 3.31		av 0.208	av 6.29
		Part B[a]			
0.83	0.131	3.29	5.90	0.189	5.72
1.04	0.145	3.10	6.11	0.183	5.90
2.08	0.255	3.28	6.28	0.192	5.85
3.12	0.355	3.29	6.53	0.194	5.89
4.16	0.440	3.23	7.05	0.200	6.19
4.68	0.490	3.28	7.15	0.201	6.13
		av 3.25		av 0.193	av 5.94

[a] $[2]_0 = 1.53 \times 10^{-4}$ M; part A, without added salt; part B, $\mu = 0.05$ M. [b] OD at infinity; 1-cm path length. Estimated limit of error ±2.0%. [c] Calculated from eq 1, with the assumption of $\epsilon_{407} = 22\,400$ for 2^- and with the same limit of error as OD. [d] Estimated limit of error ±1.5%. [e] Calculated from eq 7; estimated limit of error ±3.5%. [f] Calculated from eq 6; estimated limit of error ±5.5%. [g] $[2]_0 = 3.14 \times 10^{-5}$ M.

metal methoxides (CH_3ONa, CH_3OK, and CH_3OLi) in methanol.

This paper reports the comparison of the results in these reactions with those in the reactions of 1 with the same alkoxides and also of the stabilities of various naphthalene anionic σ complexes.

Experimental Section

Materials. Compound 2 was prepared as described previously.[11] Methanol was purified over magnesium.[12] Alkoxides were prepared from alkali metals and methanol. Optical densities and ^{1}H NMR spectra were measured on a thermostated Hitachi UV-vis spectrophotometer and Varian A-60D spectrometer, respectively.

Rate Measurements. All the procedures were done as described previously.[3] Rate measurements were made at 405–408 nm.

The K_c value at 25 °C (eq 1 and 6) was calculated with CH_3ONa as follows: K_c is expressed in eq 1, where c_{MC}, c_S, and c_{CH_3ONa} are

$$K_c = \frac{c_{MC}}{c_S c_{CH_3ONa}} \qquad (1)$$

the concentrations of complex, substrate, and alkoxide at infinity, respectively. The concentration of sodium methoxide at time zero is much greater than c_{MC} and $(c_S)_0$, so c_{CH_3ONa} can be set equal to $(c_{CH_3ONa})_0$. Furthermore, c_{MC} is expressed in eq 2, where OD

$$c_{MC} = \frac{\mathrm{OD} - \epsilon_S c_0}{\epsilon_{MC} - \epsilon_S} \qquad (2)$$

is the optical density of the complex at infinity, ϵ_S is the molecular extinction coefficient of substrate [254 (407 nm) at 25 °C], ϵ_{MC} is the molecular extinction coefficient of the complex [22 300 (407 nm) at 25 °C], and c_0 is the initial concentration of substrate. Therefore, the concentration of substrate at infinity (c_S) is $c_0 - c_{MC}$. At $[CH_3ONa]_0 = 0.0096$ M and $OD_{407} = 0.133$ (Table I), $c_{MC} = 4.25 \times 10^{-6}$ M and $c_S = 1.54 \times 10^{-4} - 4.25 \times 10^{-6} = 1.49 \times 10^{-4}$ M. Accordingly, $K_c = 2.97$ M^{-1}.

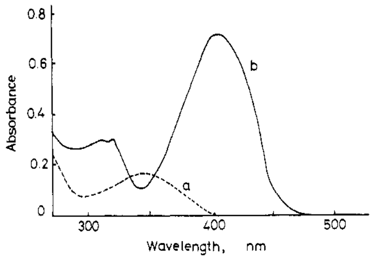

Figure 1. Spectral change relevant to the reaction of 1-methoxy-2-cyano-4-nitronaphthalene (2) with CH_3ONa in CH_3OH at 25 °C: (a) $[2]_0 = 3.15 \times 10^{-5}$ M, (b) just after addition of CH_3ONa (1.50 M).

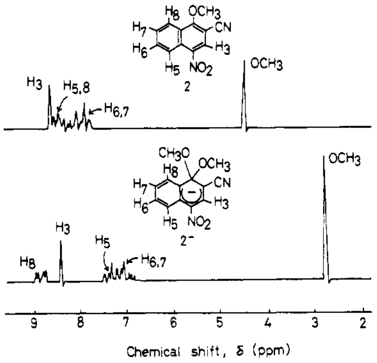

Figure 2. NMR spectral change relevant to the reaction of 1-methoxy-2-cyano-4-nitronaphthalene (2) with CH_3ONa in Me_2SO-d_6: (a) 2, (b) just after addition of 1 equiv of CH_3ONa.

Results

General Features. Upon addition of methanolic CH_3ONa (1.50 M) to 2 in CH_3OH (3.5×10^{-5} M), the solution instantly turned yellowish orange, indicating the formation of a complex (λ_{max} 407 nm, Figure 1). Proton NMR data (in Me_2SO) are also compatible with the formation of the complex 2^- (Figure 2), in which the change in signal pattern in the transformation of the substrate into the complex was similar to that in the reaction of 1-methoxy-2,4-dinitronaphthalene (3) with CH_3ONa.[4] The

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[11] Sekiguchi, S.; Hirose, T.; Tsutsumi, K.; Aizawa, T.; Shizuka, H. *J. Org. Chem.* **1979**, *44*, 3921.

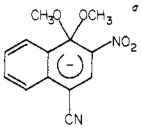
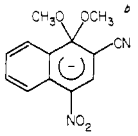
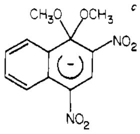
[12] Riddick, J. A.; Bunger, W. B. "Organic Solvent", 3rd ed.; Wiley-Interscience: New York, 1970; p 638.

Table II. Temperature Dependence of K_c, k_1, and k_{-1} [a]

temp, °C	K_c,[b] M^{-1}	k_1,[c] $M^{-1}\,s^{-1}$	10^2k_{-1},[d] s^{-1}
7	3.42	0.047	1.38
15	3.35	0.098	2.93
25	3.25	0.193	5.94
35	3.21	0.402	12.5

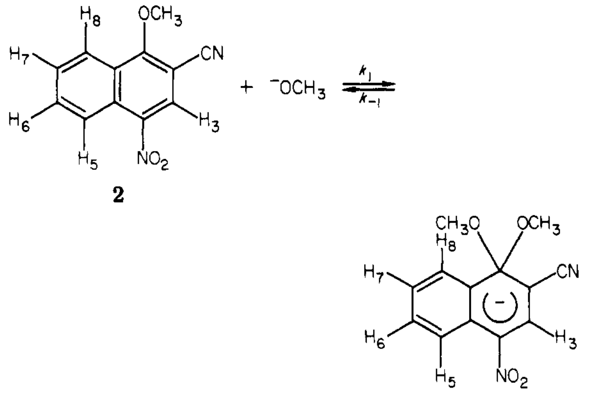
[a] μ = 0.05 M ($NaClO_4$). [b] Calculated from eq 1; estimated limit of error ±2.0%. [c] Calculated from eq 7; estimated limit of error ±3.5%. [d] Calculated from eq 6; estimated limit of error ±5.5%.

Table III. Equilibrium and Rate Constants and Thermodynamic and Activation Parameters of the Anionic σ Complexes in Methanol at 20 °C

parameter	 [a] 1^-	 [b] 2^-	 [c] 3^-
K_c, M^{-1}	14.5	3.30	230
$10k_1$, $M^{-1}\,s^{-1}$	2.11	1.52	9.00
10^2k_{-1}, s^{-1}	1.46	4.60	0.40
ΔH (K_c), kcal m^{-1}	−3.8 ± 0.3	−0.2 ± 0.8	−2.7 ± 1.6
ΔS (K_c), eu	−7.0 ± 0.4	−1.0 ± 1.1	
$\Delta H^\ddagger$ (k_1), kcal M^{-1}	12.0 ± 0.4	12.5 ± 0.2	13.2 ± 0.8
$\Delta S^\ddagger$ (k_1), eu	−21.4 ± 1.5	−20.0 ± 2.7	−17.2 ± 2.0
$\Delta H^\ddagger$ (k_{-1}), kcal M^{-1}	15.8 ± 0.7	12.7 ± 1.0	15.9 ± 0.8
$\Delta S^\ddagger$ (k_{-1}), eu	−16.0 ± 2.4	−21.4 ± 3.5	−18.0 ± 2.0

[a] Cited from ref 3. The K_c value is without ion pairing. [b] Calculated from the data in Table II. [c] Cited from ref 4 4. The K_c value is without ion pairing.

peak area of the methoxyl proton is 6 times that of H_3 in 2^-, indicating the $sp^2 \rightarrow sp^3$ change in the hybrid orbital of C-1. These results show that the reaction proceeds in the way shown in eq 3.



2

2^-

(3)

Kinetic Runs. Concentration Dependence of Rate Constants. From eq 3, the pseudo-first-order rate constant (k_ψ) is shown in eq 4. Under the present conditions

$$k_\psi = k_1([2^-] + [CH_3O^-]) + k_{-1} \tag{4}$$

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

($[CH_3O^-] \gg [2]_0$) eq 4 can be reduced to eq 5. Accordingly, the k_1 and k_{-1} values are obtained from the slope and intercept in the linear plot of k_ψ vs. $[CH_3O^-]$.

However, the k_1 and k_{-1} values in Table I were calculated in the following way. The k_1 value is represented by eq 6. Combining eq 6 with eq 5, one obtains eq 7. The k_1

$$k_1 = k_{-1}K_c \tag{6}$$

$$k_1 = \frac{k_\psi}{[CH_3O^-] + (1/K_c)} \tag{7}$$

values were derived from eq 7 by using $[CH_3ONa]$, k_ψ, and K_c (eq 1), and the k_{-1} values were obtained from eq 6 by using k_1 (eq 7) and K_c (eq 1). The apparent equilibrium constants (K_c) were derived from eq 1 by use of the extinction coefficient of 2^-.

The plots of K_c and k_ψ vs. $[CH_3ONa]$ are shown in Figure 3, which differ markedly from the corresponding plots resulting from the reaction of 1 with CH_3ONa.[3]

Table IV. Rate and Equilibrium Data for the Formation of the Anionic σ Complex from 1-Methoxy-2-cyano-4-nitronaphthalene (2) and Metal Methoxide in Methanol at 25 °C

$10^2[CH_3OM]$, M	OD	K_c, M^{-1}	10^2k_ψ,[e] s^{-1}	k_1,[f] $M^{-1}\,s^{-1}$	10^2k_{-1},[g] s^{-1}
		Part A (CH_3OK)[a]			
1.10	0.165[c]	3.20[d]	7.06	0.218	6.83
2.21	0.297[c]	3.36[d]	7.29	0.227	6.78
3.31	0.427[c]	3.49[d]	7.39	0.231	6.62
4.41	0.545[c]	3.54[d]	7.39	0.229	6.47
5.52	0.676[c]	3.70[d]	7.60	0.234	6.32
6.62	0.789[c]	3.77[d]	7.88	0.238	6.21
7.73[b]	0.478[c]	4.00[d]	8.15	0.249	6.23
8.83[b]	0.532[c]	4.06[d]	8.36	0.250	6.16
		Part B (CH_3OK)[h]			
0.89	0.184[c]	4.15[d]	6.87	0.275	6.63
1.78	0.285[c]	3.60[d]	7.22	0.244	6.78
2.68	0.388[c]	3.49[d]	7.38	0.236	6.76
3.57	0.483[c]	3.44[d]	7.78	0.239	6.95
4.46	0.582[c]	3.46[d]	7.87	0.236	6.82
		Part C (CH_3OLi)[i]			
0.75	0.133[j]	2.89[k]	7.01	0.198	6.85
1.51	0.212[j]	2.74[k]	6.98	0.184	6.72
2.26	0.273[j]	2.76[k]	7.09	0.184	6.67
3.01	0.342[j]	2.77[k]	7.38	0.189	6.82
3.77	0.409[j]	2.78[k]	7.42	0.187	6.73
4.52	0.471[j]	2.78[k]	7.74	0.191	6.87

[a] Without added salt; $[2]_0 = 1.68 \times 10^{-4}$ M. [b] $[2]_0 = 8.68 \times 10^{-5}$ M. [c] OD at infinity (408 nm); estimated limit of error ±2.0%. [d] Calculated from eq 1, with the assumption of ϵ_{MC} (408 nm) = 2.26×10^4 and ϵ_S = 219 and with the same limit of error as for OD. [e] Estimated limit of error ±1.5%. [f] Calculated from eq 7; estimated limit of error ±3.5%. [g] Calculated from eq 6; estimated limit of error ±5.5%. [h] With KCN (μ = 0.05 M); $[2]_0 = 1.81 \times 10^{-4}$ M. [i] With LiCl (μ = 0.05 M); $[2]_0 = 1.74 \times 10^{-4}$ M. [j] OD at infinity (405 nm); estimated limit of error ±2.0%. [k] Calculated from eq 1, with the assumption of $\epsilon_{MC} = 2.19 \times 10^4$ and ϵ_S = 305 and with the same limit of error as for OD.

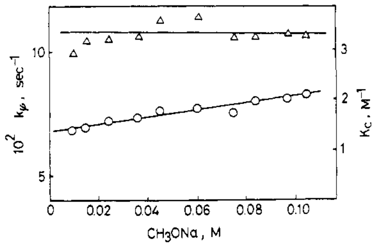


Figure 3. Relationships between k_ψ or K_c and [CH_3ONa] in the reaction of 1-methoxy-2-cyano-4-nitronaphthalene (2) with CH_3ONa in CH_3OH at 25 °C.

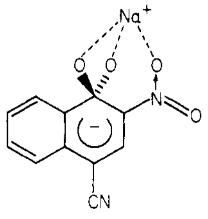
Although there was a minimum between k_ψ and [CH_3ONa] and a larger increase in K_c with increasing [CH_3ONa] in the latter, the k_ψ value increased slightly with increasing [CH_3ONa], and the K_c value was almost constant within the [CH_3ONa] investigated in the former case. A similar tendency was found in the case with the added salt (Table IB).

Temperature Dependence. The temperature dependences of k_1 and k_{-1} were determined at four temperatures (Table II). Activation and thermodynamic parameters obtained by Arrhenius plots (not shown) are listed in Table III, together with the results of Fendler et al.[4] and ours.[2]

Effects of Different Metal Methoxides. The effects of sodium, potassium, and lithium methoxides on the equilibrium and rate constants were compared with one another. The kinetic data are listed in Table IV. It can be seen that comparable K_c values are obtained with the three methoxides, whereas different results occurred in the reactions of 1 with alkoxides.[3]

Discussion

Equilibrium Constant. From the results in Tables I (part A) and IV (part A) it was found that the K_c values do not increase dramatically with increasing [CH_3ONa] or [CH_3OK] in the absence of added salts, whereas the K_c values increase with increasing [CH_3ONa] or [CH_3OK] in the reaction of 1 with CH_3ONa or CH_3OK under the same conditions.[3] The difference could be attributed to the fact that in the case of 1 the anionic σ complex (1^-) forms an ion pair ($1^-{\cdot}Na^+$, methyl groups omitted for clarity) with a counterion, Na^+ or K^+, owing to the 2-nitro group, whereas in the case of 2 the complex 2^- cannot form an ion pair. The 2-nitro group clearly plays an important role in the formation of an ion pair.



$1^-{\cdot}Na^+$

Furthermore, there is a minimum in the relationship between k_ψ and [CH_3ONa] or [CH_3OK] in the reaction of 1 with CH_3ONa or CH_3OK without added salts.[3] In contrast to this, such a minimum is not found in the reaction of 2 with CH_3ONa (Table I, part A) or CH_3OK (Table IV, part A) under the same conditions.

From Table III the K_c value decreases in the order of $3^- > 1^- > 2^-$, corresponding to the degree of charge distribution (60.60, 54.03, and 53.27% for 3^-, 1^-, and 2^-, respectively), which means the amount (percent) of negative charge delocalized over the 2- and 4-substituents of one negative charge donated by an alkoxide ion in the formation of the complex.[11] Although in the reactions of 2 with three alkoxides comparable K_c values (Tables I and IV) are obtained, larger values are obtained with CH_3ONa (14.5) and CH_3OK (9.29) and a smaller value (2.83) with CH_3OLi in the reactions of 1 with the same alkoxides.[3] Such a difference probably stems from the differences of alkoxides, which function both as added salts and as reagents.

Rate Constants and Activation Parameters. Table III shows that the electron-withdrawing substituents at the 2- and 4-positions greatly affect the K_c values, that is, the stabilities of complexes. Absence of a 2- or 4-NO_2 group considerably reduces the stability of a complex.[13,14] In comparison of 1^- and 2^-, the 2-NO_2 group clearly takes a more important role in stabilizing a complex than the 4-NO_2 group.

In the case of 3^-, its higher stability could be attributed mainly to the slowness of the reverse reaction rate, depending on $\Delta H^{\ddagger}$ (k_{-1}) as well as on $\Delta S^{\ddagger}$ (k_{-1}). With 2^- its lower stability can be ascribed to the fastness of the reverse reaction rate, depending on $\Delta H^{\ddagger}$ (k_{-1}) rather than on $\Delta S^{\ddagger}$ (k_{-1}), as compared with the case of 1^-. It can be seen, therefore, that the energy barrier of the transition state mainly governs reverse reaction rates.

In conclusion, a 2-NO_2 group in anionic σ complexes such as 1^-–3^- is necessary for formation of ion pairs. In addition, this ion pairing stabilizes the formation of the complexes.

Registry No. 1, 67122-11-6; $2{\cdot}Na^+$, 87861-47-0.

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[13] Sekiguchi, S.; Tsutsumi, K.; Shizuka, H.; Matsui, K.; Itagaki, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1521.

[14] Sekiguchi, S.; Hirose, T.; Tsutsumi, K.; Aizawa, T.; Shizuka, H. *J. Org. Chem.* **1979**, *44*, 3921.