

Aromatic Nucleophilic Substitution. 14.¹ Kinetics of the Formation and Decomposition of 1,1-Disubstituted Naphthalene Meisenheimer Complexes in the Reaction of 1-Methoxy-2-nitro-4-cyanonaphthalene with Various Metal Methoxides in Methanol. Evidence for Ion Pairing of Meisenheimer Complexes with Counterions

Shizen Sekiguchi,* Toshiaki Aizawa, and Masaru Aoki

Department of Synthetic Chemistry, University of Gunma, Kiryu, Gunma 376, Japan

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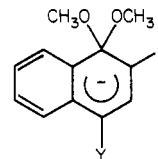
The reactions of 1-methoxy-2-nitro-4-cyanonaphthalene (1a) with various metal alkoxides have been studied. In the reaction of 1a with sodium methoxide without added salt there is a minimum in the relationship between k_{obsd} and sodium methoxide concentration, which is considered to be the result of ion pairing of an anionic σ complex with sodium ion rather than of a salt effect. The effect of sodium methoxide concentration on the rates of formation and decomposition of 1a⁻ (1,1-dimethoxy-substituted anionic σ complex of 1a) is to increase k_1 , decrease k_{-1} , and increase K_c (apparent equilibrium constant). The increase in the K_c value is largest with sodium methoxide, moderate with potassium methoxide, and negligible with lithium methoxide, which indicates ion pairing of the anionic σ complex. Replacement of the 4-nitro group by a cyano group considerably destabilizes 1a⁻ in comparison with 1d⁻ derived from 1-methoxy-2,4-dinitronaphthalene and sodium methoxide.

Anionic σ complexes (Meisenheimer complexes) have been prepared by attack of nucleophiles on polynitro aromatic compounds.² Furthermore, evidence has accumulated for a two-step mechanism for nucleophilic aromatic substitution reactions that involve such complexes as intermediates.³⁻¹⁴ Accordingly, there is interest in the stabilities and rates of formation and decomposition of such complexes.

Anionic σ complexes have been investigated in the reactions of several di-, tri-, and tetranitronaphthalenes with metal alkoxides,¹⁵⁻²⁰ and in naphthalenes.^{21,22} Complexes from mononitronaphthalenes that contain other activating

groups have not been studied.

We previously synthesized 1-methoxy-2-nitro-4-cyano (1a), 1-methoxy-2-cyano-4-nitro- (1b), and 1-methoxy-2,4-dicyanonaphthalenes (1c) and showed by UV, IR, and NMR that 1a and 1b, but not 1c, react with sodium methoxide in methanol to give the corresponding anionic σ complexes (1⁻, the minus sign representing an anionic



1a⁻, X = NO₂; Y = CN
b⁻, X = CN; Y = NO₂

σ complex).²³ It is known that the stabilities of these complexes depend on the natures of the aromatic ring, the nucleophile, the leaving group, and the solvent. We here report on the kinetics of the formation and decomposition of 1a⁻, formed by reaction of 1a with various metal alkoxides in methanol.

Experimental Section

Materials. Compound 1a was prepared as described previously.²³ Methanol was purified over magnesium.²⁴ Alkoxides were prepared from alkali metals and methanol. Optical densities were measured on a thermostated Hitachi UV-VIS spectrophotometer.

Rate Measurements. A large molar excess of alkoxide over 1a was used to assure pseudo-first-order kinetics. A standard solution of 1a (10 μ L) was injected into 2.00 mL of methanol containing excess alkoxide in a cuvette. The ionic strength was made constant by the addition of LiCl, NaClO₄, and KCN, respectively, for experiments involving lithium, sodium, and potassium methoxides. Rate measurements were made at a wavelength of 446-449 nm.

Results

General Features. The reaction of 1a with sodium methoxide in methanol at room temperature produces the

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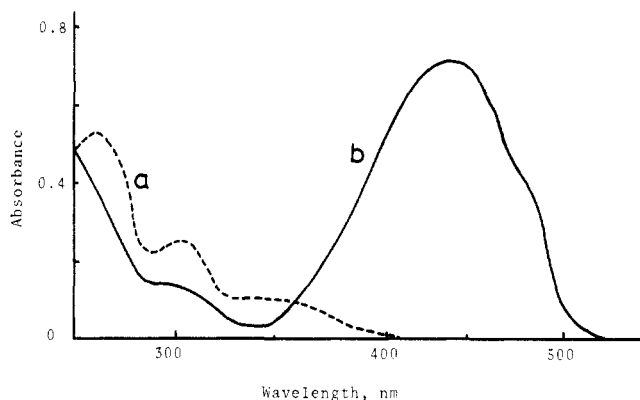
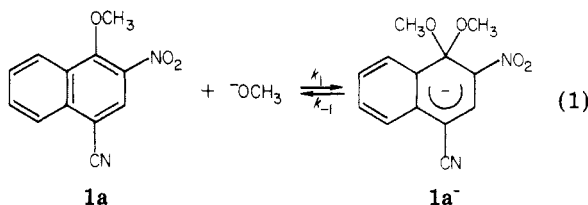


Figure 1. Spectra of the reaction of 1-methoxy-2-nitro-4-cyanonaphthalene (**1a**) with sodium methoxide in methanol: (a) $[1a] = 3.15 \times 10^{-5}$ M, $[NaOCH_3] = 8.05 \times 10^{-2}$ M; (b) **1a** just after addition of $NaOCH_3$.

anionic σ complex $1a^-$ in quantitative yield. The spectral change from curve a to curve b (Figure 1) occurred immediately upon addition of methoxide. NMR data and the assignment of absorptions based on MO calculations²³ shows that curve b is attributable to $1a^-$.

Kinetic Runs. Concentration Dependence of Rate Constants. As shown previously,²³ the complex $1a^-$ is sufficiently stable and has a large molecular extinction coefficient [λ_{max} 446 nm (ϵ 22 500)] that can be detected at concentration of $\sim 10^{-5}$ M.

The reaction process is shown in eq 1 and the apparent first-order rate constant (k_{obsd}) in eq 2. Under the con-



ditions used, $[^-OCH_3] \gg [1a]$, and consequently eq 2 can be reduced to eq 3. The rate and equilibrium data for the formation and decomposition of $1a^-$ are shown in Table I. The apparent equilibrium constants (K_c) in Table I

$$k_{obsd} = k_1([1a^-] + [^-OCH_3]) + k_{-1} \quad (2)$$

$$k_{obsd} = k_1[^-OCH_3] + k_{-1} \quad (3)$$

were derived from eq 4 by use of the extinction coefficient

$$K_c = OD/\epsilon[1a][NaOCH_3] \quad (4)$$

ϵ for $1a^-$. The value of k_1 is represented by eq 5. Com-

$$k_1 = k_{-1}K_c \quad (5)$$

binning eq 5 with eq 3, one obtains eq 6.

$$k_1 = \frac{k_{obsd}}{[^-OCH_3] + (1/K_c)} \quad (6)$$

The values of k_1 in Table I were derived from eq 6 by using $[NaOCH_3]$, k_{obsd} , and K_c (eq 4), and then those of k_{-1} were derived from eq 5 by using k_1 (eq 6) and K_c (eq 4).

The plot of K_c and k_{obsd} vs. $[NaOCH_3]$ (Table IA) is shown in Fig. 2. In the absence of added salt, there is a minimum in the relationship between k_{obsd} and $[^-OCH_3]$, which does not occur with added salt (Table IB). Figure 2 shows a nearly linear relationship between K_c and $[^-OCH_3]$, with a larger increase in K_c without added salt than with added salt (Table I). Crampton and Khan^{25,26} have reported the effect of a counterion on the ion pairing of

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

$[NaOCH_3]$, M	OD, ^b 446 nm	K_c , ^c M ⁻¹	$10^2 k_{obsd}$, ^d s ⁻¹	k_1 , ^e M ⁻¹ s ⁻¹	$10^2 k_{-1}$, ^f s ⁻¹
Part A ^a					
0.0122 ^g	0.282	7.37	3.01	0.204	2.77
0.0244 ^g	0.689	10.3	2.68	0.221	2.14
0.0427	0.277	15.0	2.60	0.238	1.58
0.0549	0.344	17.2	2.56	0.226	1.32
0.0610	0.378	18.7	2.88	0.252	1.35
0.0732	0.426	20.6	3.13	0.257	1.25
0.0976	0.504	25.2	4.01	0.292	1.16
Part B ^a					
0.0060 ^g	0.257	13.5	1.53	0.191	1.42
0.0096 ^g	0.403	13.8	1.68	0.208	1.51
0.0120	0.109	15.1	1.71	0.215	1.42
0.0241	0.182	14.3	2.06	0.219	1.53
0.0386	0.262	15.2	2.28	0.218	1.44
0.0482	0.298	15.0	2.46	0.214	1.43

^a $[1a] = 3.15 \times 10^{-5}$ M; part A, without added salt; part B, with $NaClO_4$ ($\mu = 0.05$ M). ^b OD at infinity; 1-cm path length. Estimated limit of error $\pm 2.0\%$. ^c Calculated from eq 4, with the assumption of $\epsilon_{446} = 22\,500$ for the complex and with the same limit of error as OD. ^d Estimated limit of error $\pm 1.5\%$. ^e Calculated from eq 6; estimated limit of error $\pm 3.5\%$. ^f Calculated from eq 5; estimated limit of error $\pm 5.5\%$. ^g $[1a] = 1.53 \times 10^{-4}$ M.

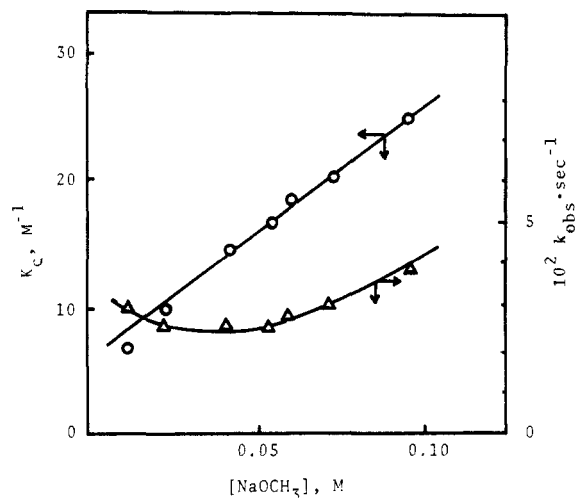


Figure 2. Dependence of k_{obsd} and K_c on $[NaOCH_3]$ in the reaction of 1-methoxy-2-nitro-4-cyanonaphthalene (**1a**) with sodium methoxide in methanol; data are from Table IA.

an anionic σ complex, where a 2-nitro group has an important influence. As will be discussed later, we believe that the minimum in k_{obsd} and the increase in K_c result from ion pairing of the anionic σ complex with a counterion.

Temperature Dependence. The temperature dependences of k_1 and k_{-1} were determined at five temperatures, with the results shown in Table II. Activation and thermodynamic parameters obtained by Arrhenius plots (Figure 3) are listed in Table III, together with the results of Fendler et al.¹⁵ on another anionic σ complex.

Effects of Different Metal Methoxides. We have compared the effects of sodium, potassium, and lithium methoxides on the equilibrium and rate constants for the

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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	$10^2 k_{-1}$, ^d s ⁻¹
15	16.6	0.0943	0.565
25	14.5	0.211	1.46
30	12.6	0.291	2.30
35	11.0	0.380	3.40
45	9.1	0.778	8.54

^a $\mu = 0.05$ M (NaClO₄). ^b Calculated from eq 4; estimated limit of error $\pm 2.0\%$. ^c Calculated from eq 6; estimated limit of error $\pm 3.5\%$. ^d Calculated limit of error $\pm 5.5\%$.

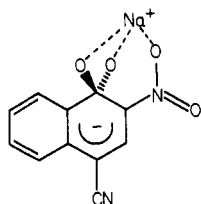
Table III. Equilibrium and Rate Constants and Thermodynamic and Activation Parameters of the Anionic σ Complex in Methanol at 25 °C

	$1a^-$	$1d^-$
K_c , M ⁻¹	14.5 ^b	230
$10^2 k_1$, M ⁻¹ s ⁻¹	2.11 ^c	9.00
$10^2 k_{-1}$, s ⁻¹	1.46 ^c	0.40
$\Delta H(K_c)$, kcal M ⁻¹	-3.8 ± 0.3^d	-2.7 ± 1.6
$\Delta S(K_c)$, eu	-7.0 ± 0.4^d	
$\Delta H^\ddagger(k_1)$, kcal M ⁻¹	12.0 ± 0.4^d	13.2 ± 0.8
$\Delta S^\ddagger(k_1)$, kcal M ⁻¹	-21.4 ± 1.5^d	-17.2 ± 2.0
$\Delta H^\ddagger(k_{-1})$, kcal M ⁻¹	15.8 ± 0.7^d	15.9 ± 0.8
$\Delta S^\ddagger(k_{-1})$, eu	-16.0 ± 2.4^d	-18.0 ± 2.0

^a See ref 15. All data are considered to be thermodynamic values. ^b K_c is the average of the equilibrium constants throughout all runs in Table IB. ^c Data from Table IB. ^d Data from Table II.

formation and decomposition of $1a^-$. The kinetic data are summarized in Table IV. In the absence of added salt, k_{obsd} for KOCH₃ goes through a minimum (Table IVA) in the same way as for NaOCH₃. Such minima were not observed for KOCH₃ with added salt and for LiOCH₃ without added salt (Table IVB,C).

The value of K_c increases with increasing [NaOCH₃] (Table IA) and increasing [KOCH₃] (Table IVA), whereas it remains almost constant with increasing [LiOCH₃] (Table IVC); these data are plotted in Figure 4. The results indicate that the size of the cation is important to ion pairing of the anionic σ complex (see below: ionic crystal radii for K⁺ = 1.33 Å, Na⁺ = 0.97 Å, and Li⁺ = 0.69 Å,²⁷ methyl groups omitted for clarity).



Discussion

Equilibrium Constant. The apparent equilibrium constants (K_c) were calculated from optical densities by use of eq 4 with an extinction coefficient ϵ of 22500 for $1a^-$. The thermodynamic equilibrium constants can be calculated from the results of the kinetics with added salt (Table IB). From the slope and intercept of the linear plot of k_{obsd} against [NaOCH₃] (not shown), we determined the values

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

[MOCH ₃], M	OD, ^d 446 nm	K_c , ^e M ⁻¹	$10^2 k_{\text{obsd}}$, ^f s ⁻¹	k_1 , M ⁻¹ s ⁻¹	$10^2 k_{-1}$, s ⁻¹
Part A (KOCH ₃) ^a					
0.0110 ^g	0.197	5.20	4.35	0.214	4.11
0.0221 ^g	0.465	6.63	4.01	0.232	3.50
0.0331 ^g	0.749	7.84	4.83	0.238	3.04
0.0441	0.338	9.71	3.78	0.257	2.65
0.0552	0.427	11.1	3.83	0.264	2.37
0.0662	0.498	12.0	4.02	0.269	2.24
0.0773	0.564	13.0	4.27	0.277	2.13
0.0883	0.626	14.2	4.53	0.285	2.01
Part B (KOCH ₃) ^b					
0.0086	0.302	10.1	3.10	0.288	2.85
0.0172	0.523	9.37	3.39	0.274	2.92
0.0258	0.711	9.01	3.57	0.261	2.90
0.0344	0.884	8.91	3.87	0.264	2.96
0.0430	1.022	8.66	4.12	0.260	3.00
Part C (LiOCH ₃) ^c					
0.0075	0.077	2.86	6.10	0.171	5.97
0.0151	0.151	2.85	6.34	0.173	6.08
0.0226	0.220	2.83	6.49	0.173	6.10
0.0301	0.288	2.84	6.69	0.175	6.16
0.0377	0.349	2.80	6.85	0.173	6.20
0.0452	0.410	2.79	6.94	0.172	6.16

^a Without added salt; [1a] = 5.17×10^{-5} M. ^b With KCN ($\mu = 0.05$ M); [1a] = 1.73×10^{-4} M. ^c Without added salt; [1a] = 1.68×10^{-4} M. ^d OD at infinity; 1-cm path length; estimated limit of error $\pm 2.0\%$. ^e Calculated from eq 4, with the assumption of $\epsilon_{446} = 21800$ for the complex and with the same limit of error as for OD. ^f Estimated limit of error $\pm 1.5\%$. ^g [1a] = 1.67×10^{-4} M.

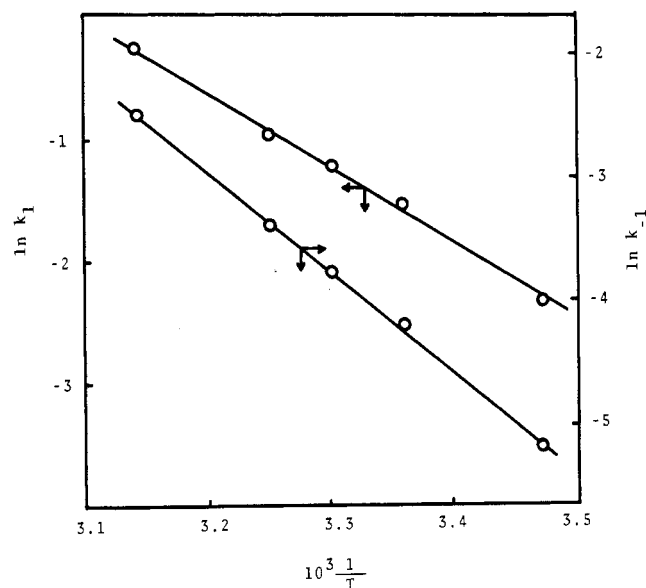


Figure 3. Arrhenius plots for k_1 and k_{-1} ; data are from Table II.

of k_1 , k_{-1} , and the thermodynamic equilibrium constants K_c shown in Table V. The values of K_c are in reasonable agreement with those shown in Table II, indicating that the reaction proceeds according to eq 1.

Ion Pairing of Anionic σ Complexes with Counterions. As already mentioned, there is a minimum in the plot of k_{obsd} and the concentration of sodium methoxide in methanol without added salt (Table IA and Figure 2). Although a salt effect has been assumed to be responsible for the minimum,²⁸⁻³¹ we propose that it arises from ion

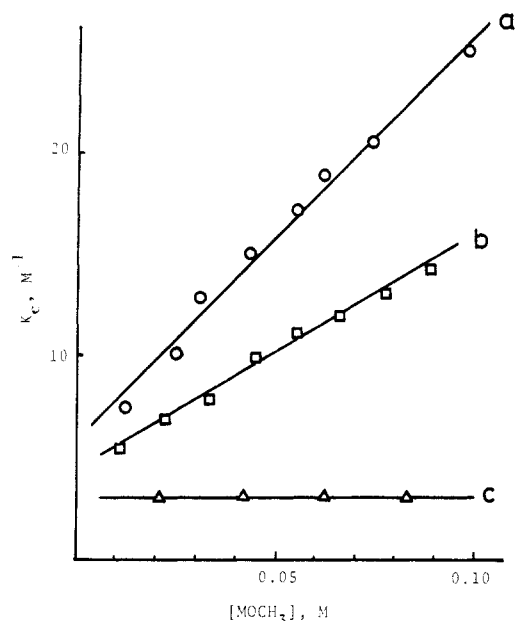


Figure 4. Relationship between K_c and $[\text{MOCH}_3]$: (a) $M = \text{Na}$, (b) $M = \text{K}$, (c) $M = \text{Li}$; data are from Tables IA, IVA, and IVC.

Table V. Values of k_f , k_{-1} , and K_c Derived from the Linear Plot of k_{obsd} vs. $[\text{NaOCH}_3]$

temp, °C	$k_f, \text{M}^{-1} \text{s}^{-1}$	k_{-1}, s^{-1}	K_c, M^{-1}
15	0.0999	0.552	18.0
25	0.214	1.46	14.7
35	0.407	3.37	12.1

pairing of an anionic σ complex with a counterion. There is evidence for ion pairing between an anionic σ complex and a counterion.^{25,26,32,33} Considering the ion association of sodium methoxide, one can write the general reaction scheme as shown in Scheme I.³⁴

Consequently, K_c and the rate constants are expressed by eq 9–11, respectively, where k_f and k_r are the rate

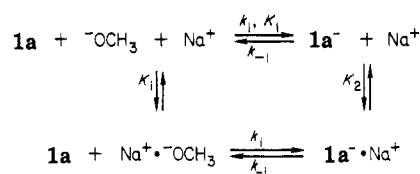
$$K_c = \frac{K_1(1 + K_2[\text{Na}^+])}{1 + K_1[\text{Na}^+]} \quad (9)$$

$$k_f = k_1 f + k_i(1 - f) \quad (10)$$

$$k_r = \frac{k_{-1} + k_{-1}K_2[\text{Na}^+]}{1 + K_2[\text{Na}^+]} \quad (11)$$

constants for the forward and reverse reactions and f and K_1 the fraction of methoxide dissociated and the association constant of methoxide. In the present experiments, the methoxide concentration was less than 0.1 M, where ion association seems not to be appreciable.³⁵ The precise value of the ion association constant of sodium methoxide is not known, but a value close to 10 M^{-1} seems likely.³⁶ Assuming this value, 98.9% of the sodium methoxide is

Scheme I



dissociated even at 0.0976 M (Table IA). Therefore, the K_1 and k_i stages could be negligible within the range of base concentration studied, so that eq 9–11 can be rewritten as eq 12–14.

$$K_c = K_1(1 + K_2[\text{Na}^+]) \quad (12)$$

$$k_f = k_1 \quad (13)$$

$$k_r = \frac{k_{-1}}{1 + K_2[\text{Na}^+]} \quad (14)$$

Furthermore, with base as the excess component, the pseudo-first-order rate constant (k_{obsd}) is related by eq 15 to the forward and reverse rate constants and to the stoichiometric methoxide concentration ($[\text{NaOCH}_3] = [\text{Na}^+]$).

$$k_{\text{obsd}} = k_1[\text{NaOCH}_3] + \frac{k_{-1}}{1 + [\text{NaOCH}_3]K_2} \quad (15)$$

From the plot of K_c against $[\text{OCH}_3^-]$ (Figure 2), it seems reasonable to assume that eq 12 holds in our experiments. Consequently, we obtain 207 M^{-2} for K_1K_2 and 5.5 M^{-1} for K_1 by the least-squares method. Thus, K_2 is 37.6 M^{-1} . By substituting eq 12 into eq 6, the values of k_1 and k_{-1} are obtained by eq 16 and 17. values for K_1 and K_2 we obtain

$$k_1 = \frac{k_{\text{obsd}}}{[\text{NaOCH}_3] + \frac{1}{K_1(1 + K_2[\text{NaOCH}_3])}} \quad (16)$$

$$k_{-1} = k_1/K_1 \quad (17)$$

the following rate constants: $k_1 = 0.241 \pm 0.006 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1} = (4.38 \pm 0.11) \times 10^{-2} \text{ s}^{-1}$.

The concentration of sodium methoxide that corresponds to a minimum ($[\text{NaOCH}_3]_{\text{min}}$) in the relationship between k_{obsd} and $[\text{OCH}_3^-]$ (Figure 2) is represented by eq 18. Substituting the above values into eq 19, we calculate

$$dk_{\text{obsd}}/d[\text{NaOCH}_3] = 0 \quad (18)$$

$$[\text{NaOCH}_3]_{\text{min}} = \frac{(k_{-1}K_2/k_1) - 1}{K_2} \quad (19)$$

$[\text{NaOCH}_3]_{\text{min}} = 0.0428 \text{ M}$, in fairly good agreement with the observed value of 0.0400 M shown in Figure 2. A similar result is obtained from the data on potassium methoxide (Table IVA): $K_1 = 4.1 \text{ M}^{-1}$, $K_2 = 28.5 \text{ M}^{-1}$, $k_1 = 0.254 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = (6.20 \pm 1.57) \times 10^{-2} \text{ s}^{-1}$, and $[\text{NaOCH}_3]_{\text{min}} = 0.0575 \text{ M}$, which is also close to the observed value of 0.0500 M.

Equilibrium and Rate Constants and Activation Parameters. The K_c value for $1d^-$ is about 16 times larger than for $1a^-$ (Table III), which indicates the important role of the electron-attracting character of the 4-nitro group. Crystal structure determinations^{37,38} have shown that the

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1,1-dimethoxy- and 1,1-diethoxy-2,4,6-trinitronaphthalene anionic σ complexes have a quinoid structure, and MO calculations³⁹⁻⁴¹ have indicated that in this complex most of one negative charge donated by the alkoxy nucleophile is located over the 4-nitro group (para to the sp^3 ring carbon).

Our MO calculations^{23,42} indicate that, in the ground state (S_0) of $1d^-$, 30% of one negative charge is located over each of the 2- and 4-nitro groups, whereas in the S_0 state of $1a^-$, the 2-nitro group bears 36% of one negative charge and the 4-cyano group 18%. The difference in electron-attracting character of the 4-substituents, therefore, is considered to affect the K_c values. Similar results have been observed in other cases.⁴³⁻⁴⁶ Terrier et al.⁴⁶ isolated

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some thiophenic and selenophenic anionic σ complexes, in which the K_c values for complex formation were larger than $490 M^{-1}$. It appears that a complex must have a K_c value larger than about $200 M^{-1}$ in order to be isolated.

From Table III it is clear that the differences between the k_1 and k_{-1} values for $1a^-$ and $1d^-$ are attributable to the entropy of activation rather than to the enthalpy of activation. Here, rigorous comparison is impossible, since the data of Fendler et al. were obtained in the absence of added salt, so that ion pairing must be taken into account. The results may indicate that the transition state for the formation of $1a^-$ is more solvated than that for the formation of $1d^-$, which seems reasonable, because the negative charge donated is less delocalized in $1a^-$ than in $1d^-$, and consequently the former should be more solvated. According to the principle of microscopic reversibility, this should also be the case for the transition state for the decomposition of $1a^-$. The result, however, is the opposite, which may be due to the ion pairing of $1d^-$ with sodium ion.

Registry No. 1a, 71436-13-0; sodium methoxide, 124-41-4; methanol, 67-56-1; KOMe, 865-33-8; LiOMe, 865-34-9.

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Kinetics and Mechanism of Hydrolysis of Chloro-1,3,5-triazines. Atrazine¹

Steven J. Plust, Joseph R. Loehe, Frank J. Feher, John H. Benedict, and H. F. Herbrandson*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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Atrazine (1) in acid solution hydrolyzes through both its monoprotonated and diprotonated forms. At temperatures up to 100 °C there are only hydronium ion, hydroxide ion, and buffer catalyses; no uncatalyzed or water-catalyzed reaction with a rate constant greater than $3 \times 10^{-11} s^{-1}$ at 25 °C contributes to the hydrolysis. Phosphate buffer catalysis may be by a specific-acid-general-base mechanism. At 25 °C the minimum rate for hydrolysis in the absence of buffer catalysis is at a pH value of 6.97 with a pseudo-first-order rate constant of $1.24 \times 10^{-11} s^{-1}$. The thermodynamic pK_a value of atrazine at 20 °C is 1.62. Consideration is given to the consequences on the pK_a value and on the rates of the acid- and buffer-catalyzed reactions of protonation on the three different heterocyclic nitrogens of the triazine.

The hydrolysis of atrazine (1, 6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) through 4-(ethylamino)-6-[(1-methylethyl)amino]-1,3,5-triazin-2-ol (2) to 4-(ethylamino)-6-[(1-methylethyl)amino]-1,3,5-triazin-2-(1*H*)-one (3) is the major pathway for chemical degradation of this herbicide.² The reaction, catalyzed by both acid and base,³ has been reported to be dependent on the hy-

drogen ion activity to the 0.6 power³ and subject to buffer catalysis with acetate and citrate buffers.^{3b} Propazine [6-chloro-*N,N'*-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine], a homologue of atrazine, also has been reported to hydrolyze with a 0.6 power dependence on the hydrogen ion activity.⁴ The nonintegral dependence of the rates of hydrolysis on the hydrogen ion activity cannot be explained by any simple mechanism. Although it was reported from three different laboratories, this unusual kinetic order may have resulted from insufficient detail in the pH-rate profile. We have accomplished a more com-

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