

Kinetic Studies on the Decomposition of the Most Typical Meisenheimer Complex of Sodium 1,1-Dimethoxy-2,4,6-trinitrocyclohexadienide in Methanol

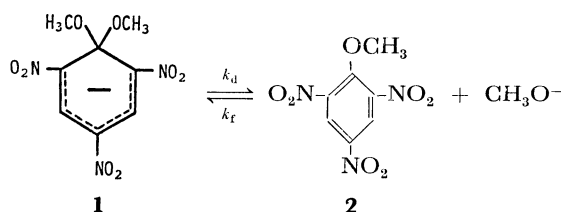
Takehiro ABE

College of General Education, Tohoku University, Kawauchi, Sendai 980

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The whole decomposition of the Meisenheimer complex formed from 2,4,6-trinitroanisole (TNA) and sodium methoxide proceeds in three steps and obeys the first-order kinetics in each step. The rate of the whole decrease of concentration of the complex is given by $-d([TNA \cdot CH_3ONa] + [TNA \cdot CH_3O^-])/dt = (k_1[H^+] + k_2[CH_3OH]) \times [TNA \cdot CH_3ONa] + (k_3[H^+] + k_4[CH_3OH]) \times [TNA \cdot CH_3O^-] - k_5[CH_3O^-] \times [TNA]$, where k denotes a rate constant. This leads to the modification of the conventional unimolecular mechanism shown by $TNA \cdot CH_3O^- \rightarrow TNA + CH_3O^-$.

The decomposition of the most typical Meisenheimer complex (**1**) formed from 2,4,6-trinitroanisole (**2**) and methoxide ion has been widely considered to be unimolecular as follows:¹⁾



Here k denotes a rate constant. The values of k_d for the decomposition of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide (**1**) have been directly measured by dissolving appropriate quantities of the sodium or potassium salt of **1** in methanol.^{2,3)} The value ($2.02 \times 10^{-3} \text{ s}^{-1}$) measured by Abe *et al.*²⁾ for k_d at 25 °C is twice that ($1.04 \times 10^{-3} \text{ s}^{-1}$) of Fendler *et al.*³⁾ An attempt has, therefore, been made to reinvestigate the decomposition of the sodium salt of **1**. This will serve to elucidate the decomposition mechanisms of all the Meisenheimer complexes.

The k_d values have also been indirectly estimated by measuring the apparent pseudo-first-order rate constants (k_{obsd}) for the formation of **1** at various methoxide concentrations much higher than that of **2**, since $k_{\text{obsd}} = k_f[CH_3ONa] + k_d$.^{3,4)} This indirect estimation is, however, unfavorable in obtaining the precise values of k_d , because the estimation leads to noticeable error because of its very small value and **1** associates with cations such as Na^+ , K^+ , Ba^{2+} and Ca^{2+} .⁵⁻⁷⁾ At room temperature, the potassium salt of **1** was more easily crystallized from a methanolic solution than the sodium salt of **1**, while the former was less easily dissolved in methanol than the latter. The lithium salt of **1** could not be crystallized from a methanolic solution. The sodium salt of **1** is, therefore, the most appropriate for the present purpose. In comparison with the cases of the potassium salt, the decomposition of the sodium salt of **1** in methanol will be reinvestigated with the help of the results of the decompositions of the sodium salt in buffer solutions and in methanolic solutions containing sodium chloride, crown ether or dimethyl sulfoxide (DMSO).

Experimental

The sodium and potassium salts of **1** were crystallized from methanolic solutions resulting from adding methanolic solutions of sodium and potassium methoxide, respectively, into methanolic solutions of **2**. The IR and NMR spectra of the salts agreed with those of literatures.¹⁾

The methanolic solutions of the salts showed strong bands at 410–415 nm. The decompositions of the appropriate quantities of the salts in solutions were followed by measuring the absorbances (A) at 420 nm with a Hitachi 100-60 spectrophotometer equipped with a thermostated cell compartment and with a Hitachi 056 recorder (path length, 1.00 cm). In the present work, the rate of decrease of A vs. t has been obtained as a decomposition rate in order to discuss the decomposition mechanism easily by the rate of decrease of concentrations of the colored species. The decomposition rate is given by dA/dt which was obtained from a recorded A vs. t (time) curve according to $(A_{-\Delta t} - A_{\Delta t})/2\Delta t$. According to the required magnitude of the error in calculating $(A_{-\Delta t} - A_{\Delta t})$, the value of Δt was often taken from 30 s to 5 min in each run. All the linear relationships between the rates and other data were obtained by the least-squares method. All the errors indicated are probable errors with the 50% significance level.

The pH values of buffer solutions (KH_2PO_4 -NaOH) of Tokyo Kasei were determined at 20.0 °C with a Hitachi-Horiba pH-meter D-5. Nisso 18-crown-6 (extra pure) was used without further purification.

Results

Decompositions of the Sodium and Potassium Salts of **1** in Methanol.

The rates for four representative runs of decomposition of the sodium salt of **1** are shown in Fig. 1. In each run the rate and absorbance become low with time. The initial concentration of the salt varies with the runs of a, b, c and d. The error in the calculation of dA/dt for $A > 1$ is twice that for $A < 1$, because the absorbances higher than 1 were recorded on a half-reduced scale. Figure 1 shows that the decomposition of the salt in methanol apparently proceeds in three steps and obeys the first-order kinetics in each step. Of course, the plot of $\ln A$ vs. t for each run similarly gave the three first-order rate constants. The rate constants of k_A , k_B , and k_C for the first, second, and third steps, respectively, are listed in Table 1. These constants obtained from the results of six runs were independent of the initial

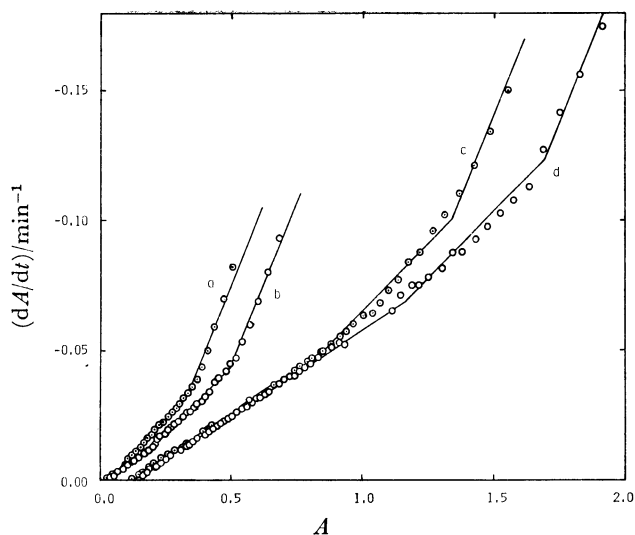


Fig. 1. Plots of dA/dt vs. A for the decomposition of the sodium salt of **1** in methanol (25.0 °C).

The initial concentrations of the salt: a; 2.4×10^{-5} M, b; 3.1×10^{-5} M, c; 7.0×10^{-5} M, d; 8.4×10^{-5} M.

TABLE I. APPARENT RATE CONSTANTS OF k_A , k_B , AND k_C FOR THE DECOMPOSITIONS OF SODIUM SALT OF **1** IN METHANOL AND IN THE METHANOL CONTAINING DMSO (25.0 °C)

Mole fraction of DMSO	$k_A/10^{-3} \text{ s}^{-1}$	$k_B/10^{-3} \text{ s}^{-1}$	$k_C/10^{-3} \text{ s}^{-1}$
0	4.2 ± 0.3	1.7 ± 0.1	1.1 ± 0.1
0.0594	2.9 ± 0.2	1.3 ± 0.1	0.83 ± 0.03
0.1243	3.0 ± 0.2	0.83 ± 0.01	0.46 ± 0.03
0.1949	1.3 ± 0.1	0.57 ± 0.03	0.30 ± 0.02

concentrations of the salt whose absorbances were below 2. The values of k_B and k_C correspond to those of Abe *et al.*²⁾ and of Fendler *et al.*,³⁾ respectively.

The decomposition of the potassium salt of **1** in methanol gave the similar results to those of the sodium salt. The rate constants (25.0 °C) obtained from four runs for the potassium salt are $k_A = (3.2 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$, $k_B = (1.7 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ and $k_C = (1.3 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$. In this case the initial decreases in absorbance could not be recorded so early as those of the sodium salt, because the potassium salt was not easily dissolved as mentioned above. Therefore, the low value of k_A for the potassium salt compared with that for the sodium salt is not decisive.

Decomposition of the Sodium Salt of 1 in Methanol Containing Sodium Chloride. The decomposition of the sodium salt of **1** in the methanol containing sodium chloride (1.02×10^{-2} M (1 M = 1 mol dm⁻³)) was the same as that of the salt in methanol without sodium chloride.

Owing to the poor solubility of sodium chloride in methanol, the concentration of sodium chloride could not be higher than 10^{-2} M. Four runs at 25.0 °C gave $k_A = (4.0 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$, $k_B = (1.8 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ and $k_C = (1.2 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$.

From the $\ln A-t$ curves of the slow decompositions of the sodium salt of **1** in methanol at *ca.* 5 °C, the

molar absorption coefficient of **1** in methanol was roughly estimated as $2.5 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$ at 420 nm by the extrapolation of the curve to the intercept. By using the coefficient value, the concentrations of the salts in the present study were estimated to be in the order of 10^{-5} M. Accordingly, the concentration of sodium chloride (1.02×10^{-2} M) was very higher than that of the sodium salt of **1**. In comparison with the results of the decomposition of the salt without sodium chloride, the presence of a small amount of sodium ion (1.02×10^{-2} M) does not apparently affect the decomposition of the salt. Fendler *et al.*⁸⁾ have, however, reported that the presence of excess sodium or potassium ion (2 M) slightly decreases the rates for the decomposition of **1** in water (pH=10.8).

Decompositions of the Sodium and Potassium Salts of 1 in Buffer Solutions. Figure 2 shows that all the decompositions of the sodium salt in the buffer solutions apparently proceed in the first and second steps for which the first-order rate constants of k_I and k_{II} can be given, respectively.

In the case of the same buffer solution (pH=7.03), k_I and k_{II} were independent of the initial concentrations of the salt. The decomposition of the sodium salt of **1** in the buffer solution (pH=7.03) afforded a yellowish crude substance after evaporation and extraction with diethyl ether. The IR spectrum of the crude substance exhibited the absorption bands corresponding to **2**. The thin-layer chromatography of the diethyl ether solution of the substance showed the presence of **2** and of a trace of picric acid. The picric acid probably resulted from the further

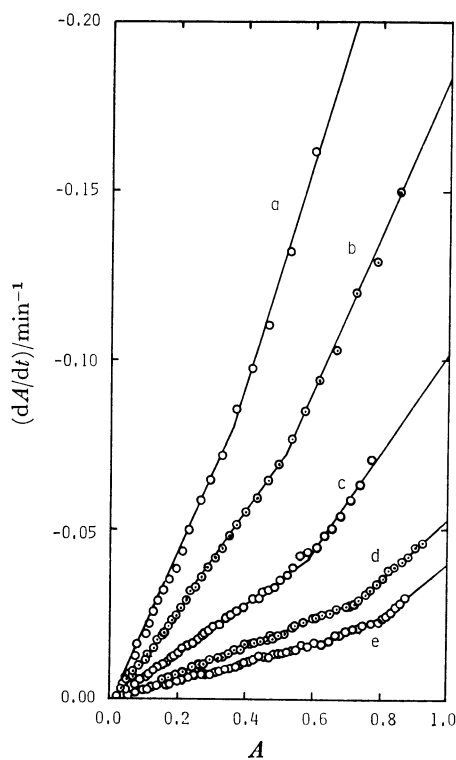


Fig. 2. Plots of dA/dt vs. A for the decomposition of the sodium salt of **1** in buffer solutions (20.0 °C). The values of pH: a; 6.04, b; 6.23, c; 6.61, d; 7.03, e; 7.40.

reaction of **2** with hydroxide ion.¹⁾

The decompositions of the potassium salt of **1** in the buffer solutions (pH=6.04, 6.23, and 6.61) gave the values of k_I and k_{II} roughly equal to the corresponding constants for the sodium salt.

Figure 3 shows that there is a linear relationship between k_I and k_{II} as follows:

$$k_I = (8.3 \pm 0.6) \times 10^{-4} \text{ s}^{-1} + (1.2 \pm 0.1) \times k_{II}. \quad (1)$$

As shown in Fig. 4, both k_I and k_{II} are linearly proportional to the proton concentration of the buffer solution. The intersections of the straight lines at $[\text{H}^+] = 0$, i.e., $k_I = (1.2 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ and $k_{II} = (2.9 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$ mean that the colored species react with not only H^+ but also water molecules (protic solvent molecules). However, even after 30 min the sodium salt of **1** showed the spectra quite identical to the initial ones in the aprotic solvents of DMSO, *N,N*-dimethylformamide, acetonitrile, and acetone. In order to make sure that no decompositions occurred prior to records of the initial spectra, conformity to Beer's law was confirmed for the DMSO solution of the sodium salt.

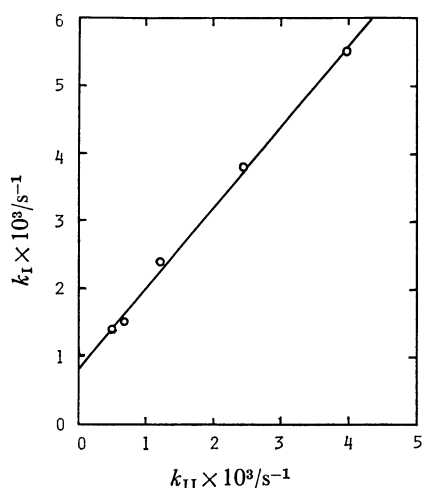


Fig. 3. Correlation of k_I with k_{II} for the sodium salt of **1** (20.0 °C).

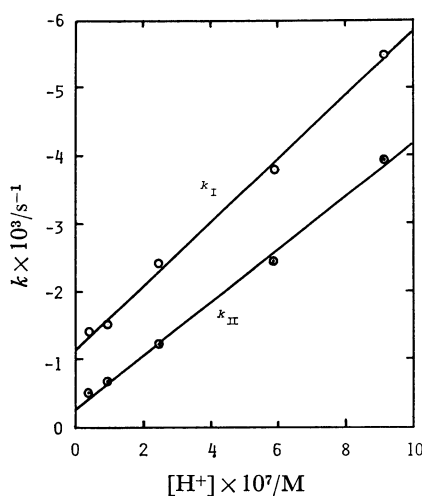


Fig. 4. Correlations of k_I and k_{II} with $[\text{H}^+]$ for the sodium salt of **1** (20.0 °C).

In the case of the potassium salt, both k_I and k_{II} were also proportional to $[\text{H}^+]$, although there were only three plots for each set of k_I and k_{II} . The plots of k_{II} were roughly similar to those for the sodium salt, while the plots of k_I were considerably scattered because of the hard solubility of the potassium salt.

Decompositions of Sodium and Potassium Salts of 1 in Methanol Containing Crown Ether. The sodium salt of **1** was decomposed at 25.0 °C in the methanolic solutions of 18-crown-6 at the concentrations of 4.8×10^{-4} , 2.13×10^{-3} , 6.43×10^{-3} , and 1.37×10^{-2} M. Representative examples for the decomposition rates are shown in Figs. 5 and 6. In the case of 2.13×10^{-3} M the whole decomposition of each run could be divided into three steps in a similar way to that in Fig. 5, while that in the case of 6.43×10^{-3} M was similar to that in Fig. 6. As shown in Fig. 5, the decomposition rates of the second and third steps are high with the decreasing initial concentration of the salt, though the concentration of the crown ether is constant. All the initial decompositions obeyed the first-order kinetics. As shown in Fig. 7, the initial first-order rate constant k_{init} is proportional to the initial concentration of 18-crown-6 ($[\text{18-Crown-6}]_0$).

The decompositions of the potassium salt of **1** in the methanolic solutions of 18-crown-6 at the concentrations of 4.8×10^{-4} , 2.13×10^{-3} and 6.43×10^{-3} M were roughly similar to the corresponding ones for the sodium salt.

Decompositions of the Sodium Salt of 1 in Methanolic Solutions Containing DMSO. The sodium salt of **1** was decomposed in the methanolic solutions containing 10, 20, and 30% (v/v) DMSO. Each decom-

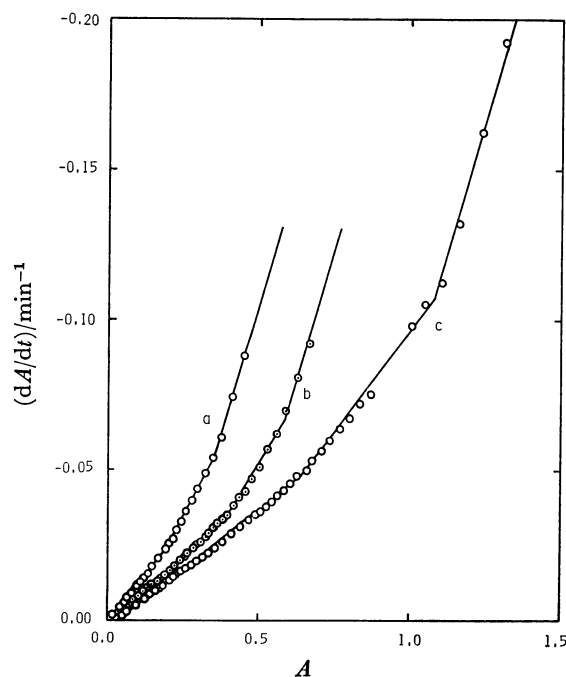


Fig. 5. Plots of dA/dt vs. A for the decomposition of the sodium salt of **1** in the methanol containing 18-crown-6 (4.8×10^{-4} M) (25.0 °C). The initial concentrations of the salt: a; 2.2×10^{-5} M, b; 3.1×10^{-5} M, c; 6.1×10^{-5} M.

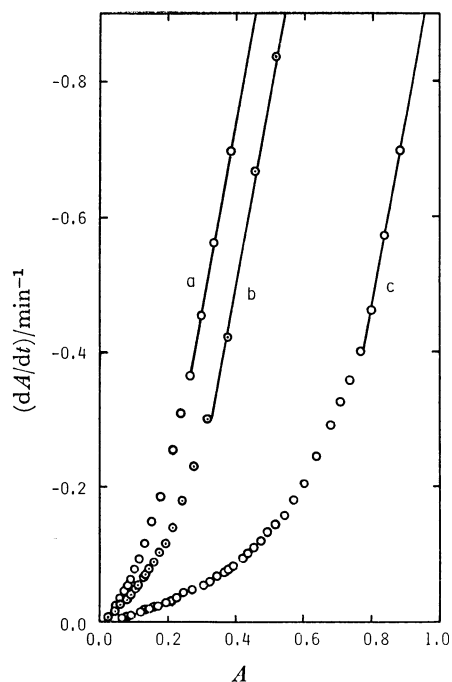


Fig. 6. Plots of dA/dt vs. A for the decomposition of the sodium salt of **1** in the methanol containing 18-crown-6 (1.37×10^{-2} M) (25.0°C). The initial concentrations of the salt: a; 3.1×10^{-5} M, b; 3.6×10^{-5} M, c; 5.1×10^{-5} M.

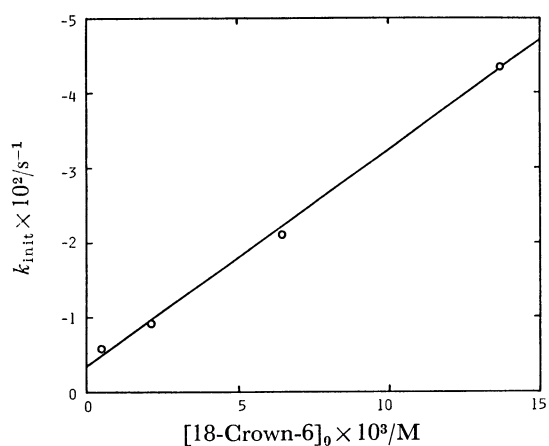


Fig. 7. Correlation of k_{init} with $[18\text{-Crown-6}]_0$ for the sodium salt of **1** (25.0°C).

position proceeded in three steps like that of the salt in methanol. The apparent rate constants obtained from three or four runs for each DMSO solution are listed in Table 1. The plots of the rate constants against the mole fractions of DMSO (x_{DMSO}) are shown in Fig. 8. There is a linear relationship between the intersections (k_i°) and slopes of the three lines of Fig. 8 as follows:

$$k_i = k_i^\circ + [(1.02 \pm 0.03) \times 10^{-3} \text{ s}^{-1} - (3.02 \pm 0.01) \times k_i^\circ] \times x_{\text{DMSO}} \quad (2)$$

where $i=A, B, \text{ or } C$. The term in the bracket on the right hand side of Eq. 2 is the slope of the i th line. Of course, k_i° corresponds to the i th rate constant for the decomposition of the salt in methanol. A

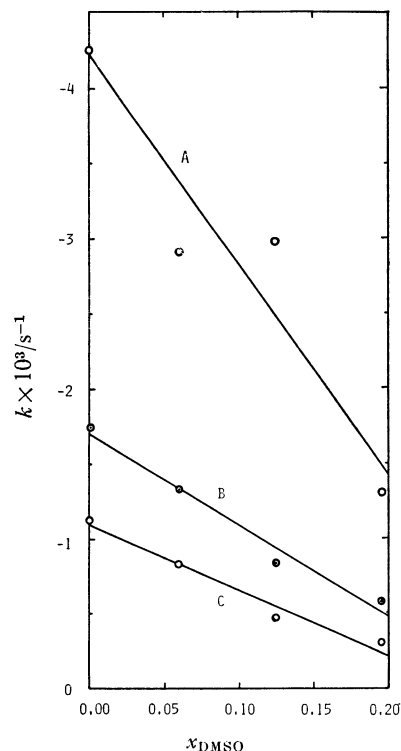
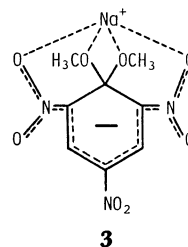


Fig. 8. Correlations of k_A , k_B , and k_C with x_{DMSO} for the sodium salt of **1** (25.0°C).

good linear relationship has been found between the logarithmic values of apparent rate constants and x_{DMSO} for the decomposition of **1** in aqueous solutions containing DMSO.⁹⁾ In the present case, there was also a good relationship between $\log k_i$ and x_{DMSO} , but the relationship corresponding to Eq. 2 was very poor.

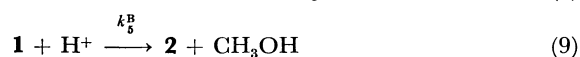
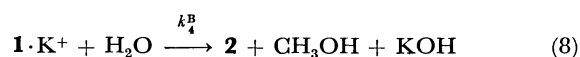
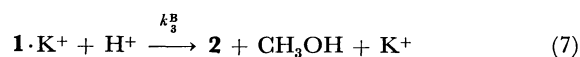
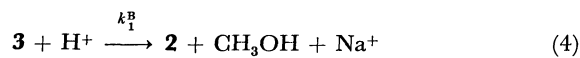
Discussion

According to the crystal structure determination of the potassium salt of **1**,¹⁰⁾ the potassium ion is located close to two oxygen atoms of the C_1 -methoxyl groups and to an oxygen atom of the C_2 - or C_6 -nitro group. Crampton and Khan^{5-7,11)} have reported the ion-pair (**3**) formed from **1** and its counter ion even in the solution, where the cation is probably held by the four oxygen atoms of the methoxyl groups and σ -nitro groups.



The appearance of the two steps in the decompositions of the salts in the buffer solutions (Fig. 2) needs to be interpreted to be due to the decompositions of both **1** and **3**, because the reformation of Meisenheimer complexes can be neglected in such buffer solutions. From the results of the decomposi-

tions of the salts in the buffer solutions ($\text{KH}_2\text{PO}_4\text{-NaOH}$), the decomposition mechanism can be written as Scheme 1. Here K denotes an equilibrium constant.



Scheme 1.

The absorbance observed at 420 nm was the sum of those of the colored species in the solution. Scheme 1 gives the rate of the total decrease of concentrations of $\mathbf{1}$, $\mathbf{3}$, and $\mathbf{1} \cdot \text{K}^+$ as follows:

$$-\frac{d}{dt}([\mathbf{1}] + [\mathbf{3}] + [\mathbf{1} \cdot \text{K}^+]) = (k_1^B[\text{H}^+] + k_2^B[\text{H}_2\text{O}]) \times [\mathbf{3}] + (k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}]) \times [\mathbf{1} \cdot \text{K}^+] + (k_5^B[\text{H}^+] + k_6^B[\text{H}_2\text{O}]) \times [\mathbf{1}]. \quad (11)$$

In the buffer solution, $[\text{H}^+]$ and $[\text{H}_2\text{O}]$ are constant. In the present study, the equal molar absorption coefficients are conveniently assumed for all $\mathbf{1}$, $\mathbf{3}$, and $\mathbf{1} \cdot \text{K}^+$, as made by Crampton and Khan.⁵⁾ Here one assumes the following relations:

$$k_1^B[\text{H}^+] + k_2^B[\text{H}_2\text{O}] = k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}] + \Delta_1$$

$$k_5^B[\text{H}^+] + k_6^B[\text{H}_2\text{O}] = k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}] + \Delta_2$$

where Δ_1 and Δ_2 are constant. Then, Eq. 11 can be written as

$$-\frac{dA}{dt} = \left[(k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}]) + \Delta_1 \right] \times \left(1 + \frac{K_1^B K_2^B [\text{K}^+]}{[\text{Na}^+]} + \frac{K_1^B}{[\text{Na}^+]} \right)^{-1} + \Delta_2 \times \left(1 + \frac{[\text{Na}^+]}{K_1^B K_2^B [\text{K}^+]} + \frac{1}{K_2^B [\text{K}^+]} \right)^{-1} \times A. \quad (12)$$

Since $[\text{Na}^+]$ and $[\text{K}^+]$ can be assumed to be constant in the same buffer solution, Eq. 12 is reduced to

$$-\frac{dA}{dt} = (k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}] + \Delta_1) \times A, \quad (13)$$

where

$$\Delta_1 = \Delta_1 \times \left(1 + \frac{K_1^B K_2^B [\text{K}^+]}{[\text{Na}^+]} + \frac{K_1^B}{[\text{Na}^+]} \right)^{-1} + \Delta_2 \times \left(1 + \frac{[\text{Na}^+]}{K_1^B K_2^B [\text{K}^+]} + \frac{1}{K_2^B [\text{K}^+]} \right)^{-1}.$$

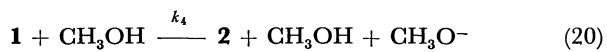
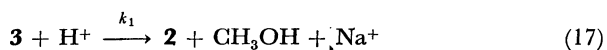
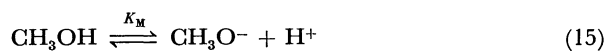
The value of $[\text{Na}^+]$ varies with the pH value of the buffer solution. The contribution of Δ_1 is, however,

probably small compared with $k_3^B[\text{H}^+]$ and $k_4^B[\text{H}_2\text{O}]$ in Eq. 13, because $\mathbf{1}$, $\mathbf{3}$, and $\mathbf{1} \cdot \text{K}^+$ are the same complexes of $\mathbf{1}$ and both Δ_1 and Δ_2 are probably small. Then, Δ_1 may be approximately assumed to be constant for all the buffer solutions. The value of $(k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}] + \Delta_1)$ corresponds to k_I . In the second step (Eqs. 6–10), $\mathbf{3}$ may vanish in the reaction system. Accordingly, the following final equation can be obtained in the same way as above:

$$-\frac{dA}{dt} = (k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}] + \Delta_{II}) \times A, \quad (14)$$

where Δ_{II} is approximately constant for all the buffer solutions. The value of $(k_3^B[\text{H}^+] + k_4^B[\text{H}_2\text{O}] + \Delta_{II})$ corresponds to k_{II} . Thus, the appearance of the two steps in the decompositions of the sodium salt of $\mathbf{1}$ in the buffer solutions can be accounted for. The empirical equation 1 may be explained by $k_I = (\Delta_1 - \Delta_{II}) + k_{II}$. The deviation of the coefficient 1.2 of k_{II} in Eq. 1 from 1 may be due mainly to an experimental error. Equations 13 and 14 show that both k_I and k_{II} should be proportional to the proton concentration in the buffer solution. In Fig. 4 the two straight lines are not completely parallel with each other, but the linear relationship between k_I and k_{II} is found in Fig. 3. The incompletely parallel lines in Fig. 4 seem to be due mainly to the pH dependences of Δ_1 and Δ_{II} .

With the help of the results of the decompositions of the salts of $\mathbf{1}$ in the buffer solutions, the decomposition mechanism of the sodium salt of $\mathbf{1}$ in methanol can be written as shown in Scheme 2. The formation



Scheme 2.

of $\mathbf{3}$ from $\mathbf{1}$ and Na^+ may be essentially neglected, because the effect of the ion pairing has been considered to be small at the cation concentration below 10^{-3} M.⁶⁾ In the first and second steps $[\text{CH}_3\text{O}^-]$ may be neglected, because it is very low in these steps and may be consumed by the carbon dioxide dissolved in the reaction system not degassed. In the reaction system $[\text{H}^+]$ may be assumed to be stationary, because the rate of the reaction ($\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^- + \text{H}^+$) can be expected to be lower than those of the ionic reactions such as $\mathbf{1} + \text{H}^+ \rightarrow \mathbf{2} + \text{CH}_3\text{OH}$ and $\mathbf{3} + \text{H}^+ \rightarrow \mathbf{2} + \text{CH}_3\text{OH} + \text{Na}^+$.

The rate of decrease of concentrations of $\mathbf{1}$ and $\mathbf{3}$ for the first step (Eqs. 15–20) is written as

$$-\frac{d}{dt}([\mathbf{1}] + [\mathbf{3}]) = (k_1[\text{H}^+] + k_2[\text{CH}_3\text{OH}]) \times [\mathbf{3}] + (k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}]) \times [\mathbf{1}]. \quad (22)$$

Here one writes the following equation:

$$k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}] = k_1[\text{H}^+] + k_2[\text{CH}_3\text{OH}] + \Delta, \quad (23)$$

where Δ is a constant. Using Eq. 23, one can reduce Eq. 22 to:

$$-\frac{d\Delta}{dt} = (k_1[\text{H}^+] + k_2[\text{CH}_3\text{OH}] + \Delta') \times \Delta, \quad (24)$$

where

$$\Delta' = \Delta \times (1 + [\text{Na}^+]/K_1)^{-1}. \quad (25)$$

Here Δ' may be approximately constant, because the value of $[\text{Na}^+]$ is very small, though it increases with time. Then, k_A corresponds to:

$$k_A = k_1[\text{H}^+] + k_2[\text{CH}_3\text{OH}] + \Delta'. \quad (26)$$

Strictly speaking, Δ' is expected to be high with decreasing initial concentration of the salt, because $[\text{Na}^+]$ is low with the decreasing initial concentration. The value of k_A may, therefore, be high to some extent with the decreasing initial concentration. This behavior seems to appear in Fig. 1, since the initial plots for the runs of a and b slope more than the straight lines of k_A , while those of c and d are reverse.

In the second step (Eqs. 15, 19, and 20), $\mathbf{3}$ may disappear in the reaction system. Accordingly, the rate of decrease of concentration of $\mathbf{1}$ for this stage may be written as

$$-\frac{d[\mathbf{1}]}{dt} = (k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}]) \times [\mathbf{1}]. \quad (27)$$

This equation can be reduced to:

$$-\frac{d\Delta}{dt} = (k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}]) \times \Delta. \quad (28)$$

Then, the rate constant of k_B is written as

$$k_B = k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}]. \quad (29)$$

In the third step (Eqs. 15 and 19–21), the reverse reaction of formation of $\mathbf{1}$ may be finally observed, because the final equilibrium absorbances of c and d are more than 0.1 in Fig. 1. From Eq. 29, the value of $k_4[\text{CH}_3\text{OH}]$ is distinctly smaller than that of k_B ($1.7 \times 10^{-3} \text{ s}^{-1}$ at 25°C). On the other hand, the rate constant ($k_5 = k_f$) for the formation of $\mathbf{1}$ is $17.3 \text{ s}^{-1} \text{ M}^{-1}$ at 25°C .³⁾ The reaction of Eq. 20 is, therefore, probably much slower than that of Eq. 21 in Scheme 2, since $[\text{CH}_3\text{OH}] = 24.6 \text{ M}$ at 25°C . Then, $[\text{CH}_3\text{O}^-]$ may be assumed to be stationary. In the third step, therefore, the decrease of $\mathbf{1}$ due to the reaction of Eq. 20 may be approximately cancelled out by the reaction of Eq. 21. Accordingly, the rate of decrease of concentration of $\mathbf{1}$ may be written as

$$-\frac{d[\mathbf{1}]}{dt} = k_3[\text{H}^+][\mathbf{1}]. \quad (30)$$

This equation leads to

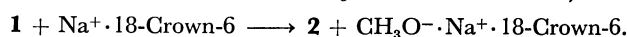
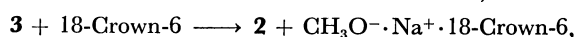
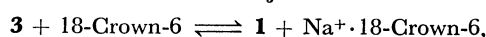
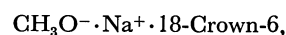
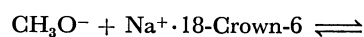
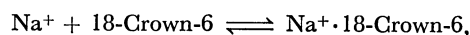
$$-\frac{d\Delta}{dt} = k_3[\text{H}^+]\Delta. \quad (31)$$

From Eq. 31, one obtains

$$k_C = k_3[\text{H}^+]. \quad (32)$$

Using the k_d value of Fendler *et al.*,³⁾ Crampton and Khan⁶⁾ have estimated the value of $1/K_1$ as 70 M^{-1} at 25°C . As Crampton and Khan have described, the value should be regarded as giving the order of magnitude of the association constant rather a precise value. Actually the calculation with the use of 70 M^{-1} leads to the unfavorable result that almost no $\mathbf{3}$ exists at the initial stage when the sodium salt of $\mathbf{1}$ is dissolved in methanol at the concentration of $5 \times 10^{-5} \text{ M}$. The precise value of $1/K_1$ will be smaller than 70 M^{-1} . Putting the value of $1/K_1$ smaller than 70 M^{-1} into Eq. 25, one can expect that only the value of k_A among k_A , k_B , and k_C becomes slightly low when the methanolic solution of the sodium salt of $\mathbf{1}$ contains the sodium chloride at the concentration of $1 \times 10^{-2} \text{ M}$, because Eqs. 29 and 32 contain no $[\text{Na}^+]$. Therefore, the experimental results of the effect of sodium chloride on the decomposition of the sodium salt of $\mathbf{1}$ may be accounted for. Thus, the appearance of the pseudo-first-order rate constants of k_A , k_B , and k_C in the decomposition of the sodium salt of $\mathbf{1}$ in methanol can be explained by Scheme 2.

The formation of ion-pairs between alkali-polyether cations and anions has been known in an organic phase.¹²⁾ In the presence of a small excess of the crown ether, sodium ions have been considered to be taken off from the Meisenheimer complexes of 1,1-dimethoxy-2-methoxycarbonyl-4,6-dinitrocyclohexadiene in methanol.¹⁴⁾ Figure 7 shows that 18-crown-6 decomposes the colored species. Accordingly, the increase in the rate of decrease of concentrations of $\mathbf{1}$ and $\mathbf{3}$ in the methanol containing 18-crown-6 seems to be due to the following additional reactions together with those of Scheme 2:



At the present time, however, the detail of the mechanism for this case can not be discussed.

The $\text{p}K_a$ value (27.9¹³⁾) of methanol in DMSO at 25°C is much larger than the logarithmic value (16.92¹⁴⁾) of the minus autoprotolysis constant of methanol. Moreover, the activity coefficient of methanol in DMSO–methanol gradually decreases with the increasing mole fraction of DMSO.¹⁵⁾ The empirical equation 2 suggests that DMSO plays the same role in all the steps. Accordingly, the decreases in the apparent rate constants of k_A , k_B , and k_C with the increasing mole fraction of DMSO (Table 1) may be due mainly to the decrease in proton concentration and partly to the decrease in activity coefficient of methanol. The decrease of proton concentration in Eqs. 26, 29, and 32 can explain the decreasing apparent rate constants (Table 1) with the increasing mole fraction of DMSO. Thus, the effects of DMSO on the decomposition of the sodium salt of $\mathbf{1}$ in DMSO–

methanol can be explained by the mechanism shown in Scheme 2.

In view of the decomposition mechanism of the salt of **1** (Scheme 2), the rate of increase of concentrations of **1** and **3** may be written for the formation of the Meisenheimer complexes from **2** and CH_3ONa in methanol as follows:

$$\frac{d}{dt}([\mathbf{1}] + [\mathbf{3}]) = k_5[\text{CH}_3\text{O}^-][\mathbf{2}] - (k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}] + \frac{\Delta}{1 + K_{-1}[\text{Na}^+]}) \times ([\mathbf{1}] + [\mathbf{3}]), \quad (33)$$

where K_{-1} is $1/K_1$. As usually made in obtaining the apparent first-order rate constants, one assumes that the initial concentration of sodium methoxide ($[\text{CH}_3\text{ONa}]_0$) is much higher than that of **2** ($[\mathbf{2}]_0$). Moreover, one assumes that $[\text{CH}_3\text{ONa}]_0$ is so low that the existence of $[\text{CH}_3\text{ONa}]$ can be ignored in the methanolic solution. Then, one can write Eq. 33 as

$$\frac{d}{dt}([\mathbf{1}] + [\mathbf{3}]) = \left(k_5[\text{CH}_3\text{ONa}]_0 + k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}] + \frac{\Delta}{1 + K_{-1}[\text{Na}^+]} \right) \times \{([\mathbf{1}]_e + [\mathbf{3}]_e) - ([\mathbf{1}] + [\mathbf{3}])\}, \quad (34)$$

where the suffix e denotes an equilibrium concentration. Here Δ and $[\text{Na}^+]$ may be approximately constant in a methoxide solution, because $[\text{H}^+]$ is very low and $[\text{CH}_3\text{ONa}]_0 \gg [\mathbf{2}]_0$. Moreover, $k_3[\text{H}^+]$ may not contribute greatly in the case of the methoxide solution, because the autoprotolysis constant of methanol is very much small.¹⁴ Therefore, the apparent pseudo-first-order rate constant k_{obsd} for the formation of the Meisenheimer complexes in methanol can be related to as follows:

$$k_{\text{obsd}} = k_5[\text{CH}_3\text{ONa}]_0 + k_3[\text{H}^+] + k_4[\text{CH}_3\text{OH}] + \frac{\Delta}{1 + K_{-1}[\text{Na}^+]}. \quad (35)$$

Among the terms on the right hand side of Eq. 35, the contribution of $k_5[\text{CH}_3\text{ONa}]_0$ is, of course, the greatest in the case of the methoxide solution. According to Eq. 35, k_{obsd} should be proportional to $[\text{CH}_3\text{ONa}]_0$. The author obtains the following good linear relationship between k_{obsd} and $[\text{CH}_3\text{ONa}]_0$ for the data observed by Fendler *et al.*³ at 410 nm in the range of $[\text{CH}_3\text{ONa}]_0$ from 1.05×10^{-3} M to 5.45×10^{-3} M:

$$k_{\text{obsd}} = (-0.4 \pm 3.8) \times 10^{-3} \text{ s}^{-1} + (18.5 \pm 1.0) \text{ s}^{-1} \times [\text{CH}_3\text{ONa}]_0. \quad (36)$$

From Eq. 33, one obtains for the equilibrium state:

$$\frac{1}{[\mathbf{1}]_e + [\mathbf{3}]_e} = \frac{1}{[\mathbf{2}]_0} + \frac{1}{k_5[\mathbf{2}]_0} \times \left(k_3[\text{H}^+]_e + k_4[\text{CH}_3\text{OH}] + \frac{\Delta_e}{1 + K_{-1}[\text{Na}^+]_e} \right) \times \frac{1}{[\text{CH}_3\text{ONa}]_0}. \quad (37)$$

Equation 37 shows that the equilibrium absorbance observed at a wavelength should be approximately proportional to $1/[\text{CH}_3\text{ONa}]_0$. This expectation is verified by using two sets of data^{4,16} as shown in Fig. 9. From the intersections of the lines of a and b in Fig. 9, one obtains the values of 2.40×10^4 and

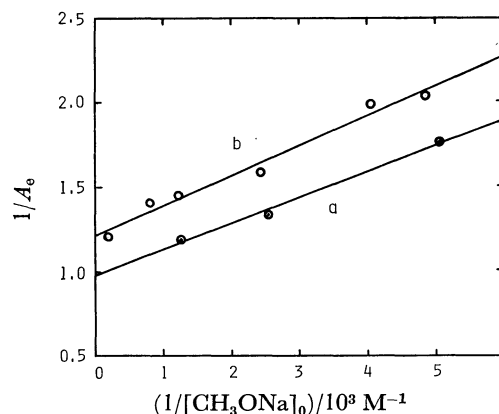


Fig. 9. Correlations of $1/A_e$ with $1/[\text{CH}_3\text{ONa}]_0$ (25 °C). The data used for the plots of a and b are taken from Refs. 4 and 16, respectively.

$2.86 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, respectively, for the molar extinction coefficient at 410 nm. These values roughly agree with the present coefficient of $2.5 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ at 420 nm.

In conclusion, the decompositions of the Meisenheimer complexes of **1** and **3** in methanol are not unimolecular, but are due to the proton resulting from the dissociation of methanol and to the protic solvent molecule of methanol as shown in Scheme 2.

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