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The Mechanism of the Reaction of 3,5-Dinitrobenzonitrile with Sodium Methoxide in Methanol

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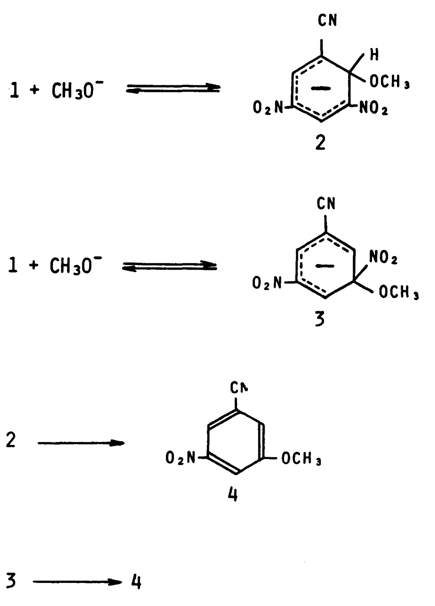
The reaction of 3,5-dinitrobenzonitrile in a methanolic solution containing a low sodium-methoxide concentration has been reinvestigated. The final product has been found to be methoxy(3,5-dinitrophenyl)methanimine, which is produced by a catalytic reaction. The reaction mechanism has been presented for the formation of the Meisenheimer complexes and the final product in the reaction system. The rate and thermodynamic stabilities for their formation have been discussed on the basis of the LUMO coefficients of 3,5-dinitrobenzonitrile and from the relative potential energies of their formation respectively, considering also the solvent effects.

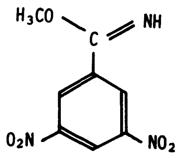
Previously Fendler *et al.*[1] proposed Scheme 1 for the reaction of 3,5-dinitrobenzonitrile (**1**) with the methoxide ion in methanol. They considered that the product (**4**) was more likely formed through **3**. Moreover, they observed the presence of the 3,5-dinitrobenzonitrile anion radical in the reaction system. The present author has been interested in their observation of the radical in connection with our work[2] on anion-radical precursors in nucleophilic substitution. The author has, therefore, reinvestigated the reaction product and, surprisingly, obtained a product different from **4**. In this paper, this product will be reported. Moreover, the reaction mechanism for the formation of the Meisenheimer complexes and product in the reaction system will be qualitatively discussed by simple theoretical treatments, taking the solvent effects into account.



Scheme 1.

Results and Discussion

The Main Product Formed from 3,5-Dinitrobenzonitrile in a Methanolic Solution Containing a Low Sodium-methoxide Concentration. The addition of a solution of **1** (*ca.* 10^{-5} mol dm^{-3}) in methanol to a methanolic solution of sodium methoxide (10^{-4}—10^{-2} mol dm^{-3}) results in the immediate formation of a red color, which however, rapidly fades.[1] The colored species showing absorption bands at 490 and 390 nm is assigned by Fendler *et al.*[1] to 1-methoxy-2-cyano-4,6-dinitrocyclohexadienide (**2**). Here, the intensity of the 490-nm band is comparable with that of the 390-nm band. These bands could be observed by fast scanning (1200 nm/min) with a usual spectrophotometer at room temperature immediately after the preparation of a methanolic solution of **1** (2.91×10^{-4} mol dm^{-3}) and CH_3ONa (8.12×10^{-3} mol dm^{-3}). These bands completely disappeared within several minutes after the preparation. However, the methanolic solution of **1** (1.95×10^{-4} mol dm^{-3}) and CH_3ONa (0.341 mol dm^{-3}) showed weak but stable absorption bands at 480, 365, and 300 nm within 5 min after the preparation. The intensity of the 480-nm band was considerably weak compared with that of the 365-nm band. The observation of the stable bands suggests the resulting product, which is not **4** but **5** (see Experimental section), further reacts with the methoxide ion to give a Meisenheimer complex like **2**, for the 480- and 365-nm bands are characteristic of 2,4-dinitrocyclohexadienide.[3] Actually, as will be described below, the isolated product (**5**) shows these bands in the presence of CH_3ONa. The pure product (**5**) could be precipitated by allowing **1** to react with a catalytic quantity of CH_3ONa in methanol and by then adding water. The catalytic reaction is quite fast, because the pure product was obtained by adding water (25 cm^3) to a methanolic solution (several cm^3) of **1** (913.4 μmol) and CH_3ONa (51.2 μmol) *ca.* 7 min after the preparation of the solution. The isolated product was identified as **5** (see Experimental section). The methanolic solution of **5** at a relatively high CH_3ONa concentration gave absorption bands at 480 and 378 nm, as is shown in Fig. 1. Their absorbances changed somewhat with the time. These bands are due probably to the formation of **6**, judging from their characteristic wavelengths and from the NMR spectrum of dimethyl sulfoxide (DMSO)-



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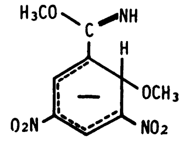

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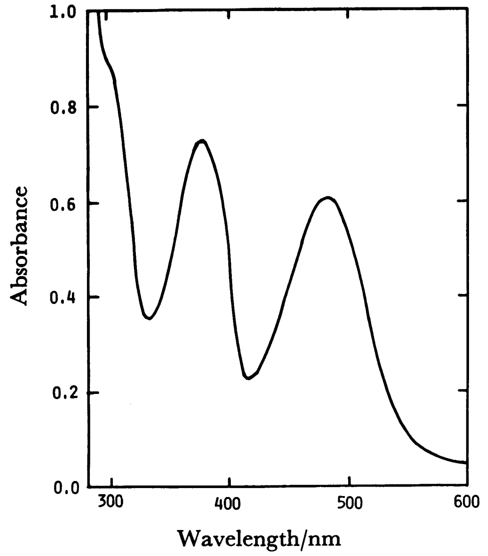
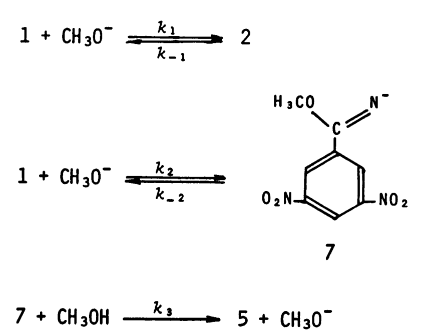


Fig. 1. Absorption spectrum of the methanolic solution of **5** (0.972 mmol dm^{-3}) and CH_3ONa (0.614 mol dm^{-3}).

d_6 solution of **5** and CH_3ONa.

The product of **5** is different from that of **4** reported by Fendler *et al.*[1] They poured the NMR sample of the isolated potassium salt of **2** (in methanol or DMSO-d_6) or of *in situ*-generated **2** (in DMSO-d_6) into water, acidified the resulting solution with HCl, and thus obtained the precipitates of **4**. If the solution diluted with water was alkaline enough, the resulting dinitrobenzene derivatives might further react in the solution, because dinitrobenzenes are apt to react in alkaline solutions. In this case, therefore, the acidification with HCl should be done before the dilution with water. In the present experiment, however, the acidification of the reddish-orange methanolic solution of **1** and CH_3ONa before the dilution with water gave a white precipitate of methyl 3,5-dinitrobenzoate. When the methanolic solution of only **5** was treated with HCl, the same precipitate was obtained. It is, therefore, obvious that the product of methyl 3,5-dinitrobenzoate obtained by the acidification of the reddish orange solution was given by the further reaction of the resulting product of **5** with HCl in methanol containing a little water. On the other hand, a similar acidification of the red solution of **1** and CH_3ONa in the DMSO containing a little methanol reproduced **1**. Thus, because of the presence of the protic solvent of methanol, **5** is produced as a stable product from the solution of **1** in the methanol containing a low CH_3ONa concentration.



Scheme 2.

*Mechanism of the Reactions of **1** in the Methanol Containing a Low CH_3ONa Concentration.* In view of the experimental finding that the methoxide ion acts as a catalyst in the formation of **5**, Scheme 2 instead of Scheme 1 is poposed for the mechanism of the reactions of **1**. At a high CH_3ONa concentration, **5** further reacts with CH_3O^- to form **6**, as has been described above. The decomposition of the most typical Meisenheimer complex of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide in methanol is considered to consist not of unimolecular, but of bimolecular reactions with proton and with methanol.[4] In the present alkaline reaction system, the reaction of **2** with H^+ may be neglected. The reverse reaction of **2** should, therefore, be written as $\mathbf{2}+CH_3OH\rightarrow\mathbf{1}+CH_3O^-+CH_3OH$. Therefore, k_{-1} contains the initial concentration of methanol, *i.e.*, $[CH_3OH]_0$, which is kept constant throughout the reaction. Similarly, the unimolecular decomposition of **7** may be written as $\mathbf{7}+CH_3OH\rightarrow\mathbf{1}+CH_3O^-+CH_3OH$, and k_{-2} may also contain $[CH_3OH]_0$.

Fendler *et al.*[1] have found that the formation of **2** in methanol attains equilibrium rapidly and that the observed pseudo-first order rate constant, k_{obsd}, for the subsequent decay of **2** is given by:

$$k_{obsd} = -\frac{d(\ln[\mathbf{2}])}{dt}. \qquad (1)$$

Moreover, they have found that k_{obsd} is related to the initial methoxide concentration $[CH_3O^-]_0$ by means of the following equation:

$$k_{obsd} = \frac{\alpha[CH_3O^-]_0}{[CH_3O^-]_0+\beta}, \qquad (2)$$

where α and β are constants. Their experimental conditions satisfy the requirements that the initial concentration of **1** (a_0) be much smaller than $[CH_3O^-]_0$ and that $[CH_3O^-]_0$ be much smaller than $[CH_3OH]_0$. Therefore, $[CH_3O^-]_0$ and $[CH_3OH]_0$ are regarded as being kept constant throughout the reaction. They obtained values of $1/\alpha$ and β/α by rearranging Eq. 2 into the expression of $[CH_3O^-]_0/k_{obsd}=\beta/\alpha+(1/\alpha)[CH_3O^-]_0$. Using their data[1] of k_{obsd} *vs.* $[CH_3O^-]_0$ at 25 °C, the present author recalculated and obtained $1/\alpha=(3.07\pm0.09)$ s and $\beta/\alpha=(1.60\pm0.02)$ mol dm^{-3} s, from which $\alpha=0.326\,s^{-1}$ and $\beta=0.521$ mol dm^{-3} were obtained.

Scheme 2 can account for Eq. 2 as follows. According to Fendler *et al.*,[1] let us assume a preliminary equilibrium for the formation of **2**, whose equilibrium constant, K_1, is written as:

$$K_1 = \frac{k_1}{k_{-2}} = \frac{[\mathbf{2}]}{[CH_3O^-]_0[\mathbf{1}]}. \qquad (3)$$

At the initial time ($t=0$), therefore, a_0 is written as:

$$a_0 = [\mathbf{1}]_0 + [\mathbf{2}]_0. \qquad (4)$$

Scheme 2 gives the following rate equations for the increases in the concentrations of **1** and **7**:

$$\frac{d[\mathbf{1}]}{dt} = -k_2[CH_3O^-]_0[\mathbf{1}] + k_{-2}[\mathbf{7}], \qquad (5)$$

$$\frac{d[\mathbf{7}]}{dt} = k_2[CH_3O^-]_0[\mathbf{1}] - (k_{-2}+k_3[CH_3OH]_0)[\mathbf{7}], \qquad (6)$$

where t denotes the time. Here let us assume the following inequality:

$$F = \frac{k_2k_3[\mathrm{CH_3OH}]_0[\mathrm{CH_3O^-}]_0}{k_2[\mathrm{CH_3O^-}]_0 + k_{-2} + k_3[\mathrm{CH_3OH}]_0} < 1\ \mathrm{s^{-1}}. \tag{7}$$

The validity of Eq. 7 will be described below. By solving Eqs. 5 and 6 simultaneously, one finally obtains the following approximate expression for [**1**]:

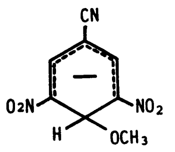
$$[\mathbf{1}] = \frac{(k_{-2} + k_3[\mathrm{CH_3OH}]_0)[\mathbf{1}]_0}{k_2[\mathrm{CH_3O^-}]_0 + k_{-2} + k_3[\mathrm{CH_3OH}]_0} \times \exp\left(-\frac{k_2k_3[\mathrm{CH_3OH}]_0[\mathrm{CH_3O^-}]_0}{k_2[\mathrm{CH_3O^-}]_0 + k_{-2} + k_3[\mathrm{CH_3OH}]_0} \times t\right). \tag{8}$$

The combination of Eqs. 1, 3, and 8 leads to:

$$k_{\mathrm{obsd}} = \frac{k_3[\mathrm{CH_3OH}]_0[\mathrm{CH_3O^-}]_0}{[\mathrm{CH_3O^-}]_0 + (k_{-2} + k_3[\mathrm{CH_3OH}]_0)/k_2}. \tag{9}$$

Equation 9 is equivalent to Eq. 2. Thus, the experimental relation of Eq. 2 can be accounted for according to Scheme 2. By comparing Eq. 9 with F in Eq. 7, one obtains the relation of $F = k_{\mathrm{obsd}}$. The k_{obsd} values measured by Fendler *et al.*[1] are less than 0.16 $\mathrm{s^{-1}}$. Therefore, the assumption of Eq. 7 is reasonable. By comparing the values of α and β with $k_3[\mathrm{CH_3OH}]_0$ and $(k_{-2}+k_3[\mathrm{CH_3OH}]_0)/k_2$ respectively in Eq. 9, one obtains $k_3 = 0.326\ \mathrm{s^{-1}}/[\mathrm{CH_3OH}]_0$ and $k_2 = (k_{-2}+0.326\ \mathrm{s^{-1}})/0.521\ \mathrm{mol\ dm^{-3}}$. From these relations for k_3 and k_2, one obtains $k_3 = 1.33 \times 10^{-2}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ at 25.0 °C ($[\mathrm{CH_3OH}]_0 = 24.55\ \mathrm{mol\ dm^{-3}}$) and may say that k_2 is larger than either k_{-2} or k_3. If the steady-state treatment is applied to the concentration of **7**, one obtains finally an expression for k_{obsd} in which the denominator of Eq. 9 is replaced by $(k_{-2}+k_3[\mathrm{CH_3OH}]_0)/k_2$. In this case, therefore, Eq. 2 cannot be accounted for.

Explanation of the Rates and Thermodynamic Stabilities of the Formations of 2, 7, and 8 by Theoretical Treatments Taking the Solvent Effect into Account. In the case of a DMSO solution containing a little methanol, not only **2**[1,5,6] but **8**[6] is observed by NMR spectroscopy. Crampton and Khan[7] reported that **8** shows an absorption band at 550 nm in the DMSO.



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Indeed, the longer absorption band characteristic of the Meisenheimer complex,[3] like **8**, was distinctly observed at 560 nm with the usual spectrophotometer when a small quantity of solid $\mathrm{CH_3ONa}$ was added to a solution of **1** in DMSO. The formation of **8** is kinetically faster, but thermodynamically less stable, than that of **2** in the DMSO.[6,7] On the other hand, **8** has never been observed in a methanolic solution containing no DMSO. However, the following findings related to the present case seem to suggest the transient formation of **8** in methanol. Terrier *et al.*[3b,6] found that the equilibrium constant for the formation of 1-hydroxy-4-cyano-2,6-dinitrocyclohexadienide from **1** and $\mathrm{OH^-}$ in a mixture of water and DMSO decreases with a decrease in the amount of DMSO, while the rate constant for the decomposition of the complex increases reversely. By a temperature-jump method, Bernasconi[8] found that the formation of 1,3-dimethoxy-2,4,6-trinitrocyclohexadienide, corresponding to **8**, proceeds even in methanol, and that the equilibrium constant for the formation of the complex is exceedingly small compared with that for 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide, corresponding to **2**, while the rate constant for the decomposition of the 1,3-dimethoxy complex is exceedingly large compared with that of the 1,1-dimethoxy complex. In view of the above findings, one may consider the transient formation of **8** in methanol on the assumptions that the equilibrium constant for the formation is very small and that the rate constant for the decomposition of **8** is quite large. Moreover, by analogy with the case of the DMSO solution, one may consider that, in methanol, the formation of **8** is kineticaly faster and thermodynamically less stable than that of **2**. Thus, one may conclude as follows: The formation of **2** is kinetically slower and thermodynamically more stable than that of **8** in both methanol and DMSO. The formation of **5** is the slowest in methanol and is not produced in the DMSO containing a little methanol.

An attempt will now be made to account for the above conclusions by drawing the potential-energy profiles against a reaction coordinate for the formations of **2**, **7**, and **8** in methanol or DMSO. The rates of these formations may be lower in the order of the increase in the activation energies, because the frequency factors of the rate constants for these formations proceeding in the identical solution of **1** and $\mathrm{CH_3O^-}$ may be regarded as approximately the same. According to the frontier orbital theory[9] and the symmetry rules[10] for chemical reactions, $\mathrm{CH_3O^-}$ may attack the atomic positions of **1** more easily in the order of their increasing absolute values of the coefficients of the lowest unoccupied molecular orbital (LUMO) for **1** on the assumption that the initial slopes of the potential-energy curves for the formations of **2**, **7**, and **8** are proportional to their activation energies. The theory and the rules have been widely accepted. Accordingly, the rates of the formations of **2**, **7**, and **8** may be lower in the order of the decrease in the coefficients of the LUMO because the activation energies increase in the same order. On the other hand, the thermodynamic stabilities of **2**, **7**, and **8** in the solution increase in the order of their decreasing potential energies and will be discussed by considering their relative potential energies.

Let us consider a neutral solute molecule with a π-electron system and a dipole moment of $\boldsymbol{p}$ (in its free state). By the use of the Onsager reaction field, the rth coefficient ($c_{\mathrm{L}r}$) of the LUMO for the π-electron system containing n core atoms is given approximately, according to a previous paper,[11] as follows:

$$c_{\mathrm{L}r} = c^{\circ}_{\mathrm{L}r} + \frac{\varepsilon_{\mathrm{r}}-1}{2\varepsilon_{\mathrm{r}}+1} \times \frac{2e\boldsymbol{p}}{a^3}\,\boldsymbol{\sigma}_{\mathrm{L}r}, \tag{10}$$

where:

$$\boldsymbol{\sigma}_{\mathrm{L}r} = \sum_{k\neq\mathrm{L}}^{\mathrm{all}} \frac{\left(\sum_{p=1}^{n} c^{\circ}_{\mathrm{L}} c^{\circ}_{kp} \boldsymbol{r}_p\right)}{\varepsilon^{\circ}_{\mathrm{L}} - \varepsilon^{\circ}_{k}}\, c^{\circ}_{kr}. \tag{11}$$

Here, e is the charge of the proton, ε_{r} is a relative permittivity of the solvent, a is a cavity radius, ε°_{k} is an energy level of the kth MO for the free solute molecule, c°_{kp} is the pth coefficient of the kth MO, and r_p is a position vector of the pth atom. The letter L denotes the LUMO. Equation 10 is written by neglecting the hydrogen-bonding effect due to a change (δa_p) in the Coulomb integral of the pth atom, because it is convenient to evaluate the effect of δa_p resulting from the hydrogen bonding between the pth atom and the solvent molecule by directly solving a secular equation taking δa_p into account using a computer. In the present case, the Onsager reaction field is used for convenience instead of the better Block and Walker reaction field for the neutral molecule,[11] since the reaction field used below for an anion is the Onsager one. As has been described in the previous paper,[11] a dispersion effect is not considered in the above treatment. Consequently, the application of Eq. 10 to a solute molecule with no permanent dipole moment or only a small one is unfavorable. In the present treatment, however, the dispersion effect on all the coefficient of the LUMO is neglected on the assumption that the small dispersion effect of the identical solvent causes no considerable changes in any of the coefficients for the identical solute molecule.

All the molecules of **2**, **7**, and **8** are anions. One considers an anion consisting of N charged particles as a whole. The energy of the ground state, Ψ°_{g}, of the anion in its free state is denoted by E°_{g}. The charge and position vector of the jth particle of the N particles are denoted by e_j and r_j respectively. As will be given in the Appendix, the reaction potential (ϕ_R) and field ($\boldsymbol{R}$) of the anion at the center of the cavity are written, respectively, as:

$$\phi_R = \frac{1-\varepsilon_r}{\varepsilon_r} \times \frac{1}{a}\left(\sum_{j=1}^{N} e_j\right), \tag{12}$$

$$\boldsymbol{R} = \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} \times \frac{2\boldsymbol{p}_g}{a^3}, \tag{13}$$

where $\boldsymbol{p}_g$ is the dipole moment of the free anion in its ground state. Here, $\sum e_j$ is $-e$ for the present anion. Both Eqs. 12 and 13 give potential energies twice the corresponding Helmholtz free energies.[12,13] According to the previous paper,[11] the perturbation for the anion in the solution can be written from Eqs. 12 and 13 as:

$$H' = \sum_{j=1}^{N} e_j(\phi_R - \boldsymbol{R}\cdot\boldsymbol{r}_j). \tag{14}$$

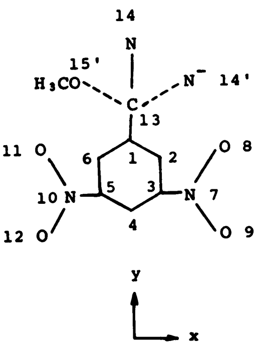
From the first-order perturbation theory, therefore, the energy, E_g, of the anion in the solution can easily be obtained as follows:

$$\begin{aligned} E_g &= E^{\circ}_g + (\Psi^{\circ *}_g|H'|\Psi^{\circ}_g) \\ &\quad + \sum_{m\neq g} \frac{(\Psi^{\circ *}_g|H'|\Psi^{\circ}_m)(\Psi^{\circ *}_m|H'|\Psi^{\circ}_g)}{E^{\circ}_g - E^{\circ}_m}, \\ &= E^{\circ}_g - \frac{\varepsilon_r - 1}{\varepsilon_r} \times \frac{e^2}{a} - \boldsymbol{R}\cdot\boldsymbol{p}_g - \frac{R^2\alpha_g}{2}, \end{aligned} \tag{15}$$

where E°_m is an energy of the mth excited state of the free anion and α_g is the isotropic polarizability of the free anion in the ground state. Here, one assumes that the differences among the E°_g values of **2**, **7**, and **8** are mainly due to their π-electronic energies of $2\sum^{\text{occu}} \varepsilon^{\circ}_k$, because their σ-bonds are approximately the same except for the bonds of CN, such as C≡N and C=N⁻. The σ-electronic energy of **7** containing the C=N⁻ bond is higher by roughly the energy (E_{C-N}) of a C–N bond than those of **2** and **8**, both containing the C≡N bonds. The magnitude of E_{C-N} is considered to be 291.6 kJ mol^{-1} of the C–N bond[14] for the relative potential energy of **7**. In the case of **2** and **8**, the energy (E_{OCH_3}) of the π-electron system of OCH_3 must be considered, because the methoxyl group of **7** participates in the π-electron system. Accordingly, from Eq. 15, the relative potential energy (E_r) being considered for the anion may be approximately written as:

$$\begin{aligned} E_r &= \Delta E + 2\sum_{k=1}^{\text{occu}} \varepsilon^{\circ}_k - \frac{\varepsilon_r - 1}{\varepsilon_r} \times \frac{e^2}{a} \\ &\quad - \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} \times \frac{2p_g^2}{a^3} - \left(\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}\right)^2 \times \frac{2p_g^2\alpha_g}{a^6} - \Delta E_H, \end{aligned} \tag{16}$$

TABLE 1. ATOMIC COORDINATES AND MOLECULAR ORBITAL PARAMETERS FOR π-ELECTRON SYSTEMS OF **1**, **2**, **7**, AND **8**

	Position	Atomic coordinates[a)]		Integrals[b)]
		x/Å	y/Å	
	1	0	1.38	$h_7 = h_{10} = 2$
	2	1.20	0.69	$h_8 = h_9 = h_{11}$
	3	1.20	−0.69	$= h_{12} = 1.5$
	4	0	−1.38	$h_{14} = 0.5$
	5	−1.20	−0.69	$h_{14'} = 0$
	6	−1.20	0.69	$h_{15'} = 2$
	7	2.47	−1.43	
	8	3.67	−1.38	$k_{3,7} = k_{5,10}$
	9	2.43	−2.62	$= k_{13,14} = {}_{13,14'}$
	10	−2.47	−1.43	$= k_{13,15'} = 0.8$
	11	−3.67	−1.38	$k_{7,8} = k_{7,9}$
	12	−2.43	−2.62	$= k_{10,11} = k_{10,12}$
	13	0	2.85	$= 0.7$
	14	0	4.01	
	14′	1.14	3.50	
	15′	−1.16	3.51	

a) 1 Å = 0.1 nm. b) Coulomb ($\alpha_r = \alpha_0 + h_r\beta_0$) and resonance ($\beta_{rs} = k_{rs}\beta_0$) integrals for the rth atom and the r–s bond respectively.

TABLE 2. VALUES OF α_r DUE TO HYDROGEN BONDINGS

Case	$\delta\alpha_8/\beta_0$	$\delta\alpha_9/\beta_0$	$\delta\alpha_{11}/\beta_0$	$\delta\alpha_{12}/\beta_0$	$\delta\alpha_{14}/\beta_0$
1	0	0	0	0	0
2	0	0	0	0	0.1
3	0.1	0	0	0	0.1
4	0.1	0	0.1	0	0
5	0.1	0	0.1	0	0.1
6	0.1	0.1	0.1	0.1	0
7	0.1	0.1	0.1	0.1	0.1

where $\Delta E = E_{\text{C-N}} + E_{\text{OCH}_3}$. Here, ΔE_H is the stabilization energy due to hydrogen bondings between the anion and protic solvent molecules.

The parameters used for the present Hückel MO calculations were taken, for the most part, from Ref. 15: They are shown in Table 1, together with the atomic coordinates based on the X-ray crystal analysis of *m*-dinitrobenzene.[16] The value of $h_{14'}$ is taken to be smaller than that (0.5) for $\dot{N}$ by 0.5, because the nitrogen atom of $C{=}N^-$ may decrease its electronegativity compared with that of $\dot{N}$ because of the presence of the negative charge on the nitrogen. Here, α_0 and β_0 denote the Coulomb and resonance integrals respectively for the carbon atom bonded to a carbon atom, where $\beta_0 = -3.00$ eV (1 eV$=9.648\times10^4$ J mol^{-1}) is assumed. The LUMO coefficients relating to the formations of **2**, **7**, and **8** are shown in the first row of Case 1 in Table 3. The row shows the relation of $c_{L4}^{\circ} > |c_{L2}^{\circ}| > c_{L13}^{\circ}$ in the case of the absence of the solvent. In order to apply Eq. 10 to **1** in methanol, the dipole moment (p) of **1** is necessary, but it can not be found. Therefore, p was estimated to be 0.07 D (1 D$=3.333\times10^{-30}$ C m) in the negative direction of the y axis from the vector sum of the dipole moments of benzonitrile (4.14 D[14]) and nitro groups (4.21 D[14]). The relative permittivities used for methanol and DMSO are 32.70 and 46.68[17] respectively at 25 °C. The relative permittivity of the solution was taken to be approximately equal to that of the solvent. The value of a was tentatively assumed to be the same value of 4.4 Å (1 Å$=0.1$ nm) as was assumed for a radius of the Meisenheimer complex of 1,3,5-trinitrobenzene with cyanide.[18] The results of calculations according to Eq. 10 are listed in the second row of Case 1 in Table 3. The row shows that the same relation of $c_{L4} > |c_{L2}| > c_{L13}$ holds for the case of the methanolic solution. This relation also holds for the case of DMSO, because the difference in the value of $(\varepsilon_r - 1)/(2\varepsilon_r + 1)$ between methanol and DMSO is very small. In a methanolic solution, however, the hydrogen bondings can be expected to be formed between **1** and methanol, because the formations of hydrogen bondings are found for the interactions of methanol with nitromethane and with acetonitrile.[19] The hydrogen bonding between methanol and acetonitrile is somewhat stronger than that between methanol and nitromethane.[19] According to the β-scale of the solvent hydrogen-bond acceptor basicities,[20] the hydrogen-acceptor ability of benzonitrile is somewhat stronger than that of nitrobenzene. In view of the above findings, Cases 2—7 in Table 2 have been selected in order to examine the effect of the hydrogen bondings. The most probable case may be either 5 or 7, because the concentration of methanol present as the solvent is extremely high. From the solvent effects on a hyperfine splitting constant in the ESR spectrum of the di-*t*-butyl nitroxide radical,[11] the value of $\delta\alpha_r$ due to the hydrogen bonding was estimated as follows: From the difference in the hyperfine splitting constants between the observed and calculated values for the solvent of methanol, the magnitude of 0.0556 mT was estimated to be due to the hydrogen bonding between methanol and the radical. The combination of the magnitude and the last term of Eq. 20 of Ref. 11 leads to $\delta\alpha_0 = 0.1\,\beta_0$, where the Hückel MO's used for the π-electron system of N=O were obtained by taking $\alpha_N = \alpha_0 + 0.5\,\beta_0$, $\alpha_O = \alpha_0 + \beta_0$, and $\beta_{NO} = \beta_0$. For convenience, therefore, $\delta\alpha_r = 0.1\,\beta_0$ was assumed for all the oxygen and nitrogen atoms of the nitro and cyano groups respectively in **1**, as is indicated in Table 2. The results of the calculations for Cases 2—7 in Table 2 are listed in Table 3. All the cases in Table 3 give the relation of $|c_{L4}| > |c_{L2}| > |c_{L13}|$. Thus, this relation may hold for the methanolic solution of **1**, even if **1** forms hydrogen bonds with the methanol molecules. As has been described above, the relation means that the activation energies of the formations of **2**, **7**, and **8** in

TABLE 3. VALUES OF c_{Lr}°, c_{Lr}, AND σ_{Lr} (y) FOR **1** IN METHANOL

Case[a)]	(c_{L2}°) c_{L2}	(c_{L4}°) c_{L4}	(c_{L13}°) c_{L13}	$\sigma_{L2}(y)/\text{Å}\beta_0^{-1}$	$\sigma_{L4}(y)/\text{Å}\beta_0^{-1}$	$\sigma_{L13}(y)/\text{Å}\beta_0^{-1}$
1	(−0.0730) −0.0716	(0.4604) 0.4595	(0.0343) 0.0326	1.7347	−1.1255	−2.1220
2	(0.0540) 0.0529	(−0.4493) −0.4485	(−0.0034) −0.0022	−1.3289	1.0521	1.4638
3	(−0.0182) −0.0169	(0.4549) 0.4540	(0.0062) 0.0049	1.6711	−1.0862	−1.5598
4	(0.0840) 0.0825	(−0.4737) −0.4728	(−0.0436) −0.0417	−1.9362	1.0817	2.4030
5	(0.0627) 0.0616	(−0.4629) −0.4620	(−0.0088) −0.0075	−1.4940	1.0745	1.6617
6	(0.0967) 0.0951	(−0.4872) −0.4865	(−0.0546) −0.0526	−2.0962	0.9078	2.6695
7	(−0.0730) −0.0718	(0.4775) 0.4767	(0.0156) 0.0141	1.6430	−0.9999	−1.8705

a) Case numbers correspond to those of Table 2.

TABLE 4. RELATIVE POTENTIAL ENERGIES OF **2**, **7**, AND **8** IN METHANOL

Anion	$(\Delta E+2\sum_{k=1}^{occu}\varepsilon_k^\circ)$	Coordinates of center of mass $(x/Å, y/Å)$	Dipole moment (Debye) obtained by setting the origin at the center of mass						p_g	$-\frac{\varepsilon_r-1}{2\varepsilon_r+1}\cdot\frac{2p_g^2}{a^3}$	E_r
			Vector sum of moments of the bonds and groups		Moment of the negative charge		Total moment				
			x	y	x	y	x	y			
2	$18\alpha_0+31.762\beta_0$	(−0.17, 0.25)	−0.53	−0.12	7.68	16.51	−8.21	−16.63	18.55	$0.802\beta_0$	$18\alpha_0+32.564\beta_0$
8	$18\alpha_0+31.858\beta_0$	(0, −0.54)	0	0.79	0	17.00	0	−16.21	16.21	$0.613\beta_0$	$18\alpha_0+32.471\beta_0$
7	$18\alpha_0+31.732\beta_0$	(−0.09, 0.11)	1.95	−4.44	−5.91	−16.28	7.86	11.84	14.22	$0.472\beta_0$	$18\alpha_0+32.204\beta_0$

methanol may be higher in the order of **2**, **8**, and **7**.

When Eq. 16 is applied to the anions of **2**, **7**, and **8**, the third term in Eq. 16 is the same for all the anions, because their charges are the same. Here, one assumes that the values of a_g and ΔE_H are approximately the same for all the anions, because their constituent atoms are the same and because, in view of their structures, their abilities to form the hydrogen bonds seem not to differ considerably. Moreover, the fifth term of Eq. 16 is smaller than the fourth one. Accordingly, the difference in the E_r values among the anions are mainly due to the first, second, and fourth terms of Eq. 16. Here, therefore, only these terms are considered as the relative potential energies (E_r). Here, $E_{C-N}=-1.007\ \beta_0$ and $E_{OCH_3}=2\alpha_0+4\beta_0$ are dropped out for **2** and **8** and for **7** respectively. The sums of the first and second terms are shown in the second column of Table 4. The total dipole moments of each anion in the directions of the x and y axes were estimated from the vector sums of two moments; the vector sum of the moments of the constituent bonds and groups and the moment of the negative charge of the anion. The vector sums obtained by using the moments[14] of the bonds and groups are shown in Table 4. The dipole moment of the anion varies with the way of setting the origin of the coordinates; the center of the mass of the anion is usually set as its origin.[18] Therefore, the moments of the negative charges of **2**, **7**, and **8** were calculated by shifting the origins at their centers of masses, shown in Table 4. The negative charge of **7** is located in the nitrogen atom of $C=N^-$ and is immediately calculated from the nitrogen coordinates. The negative charges of **2** and **8** are distributed in their π-electron systems, and their moments are equal to the π-moments. The π-moments are given by multiplying the coordinates of the centers of the negative-charge distributions by $-e$. The coordinates of each center of the distribution were calculated by using the Hückel MO's which had been obtained with the use of the parameters and coordinates in Table 1. The moments of the negative charges and the total moments are shown in Table 4. Then, each moment of p_g was obtained from the vector sum of the total x- and y-moments, as is shown in Table 4. Here, 4.4 Å was assumed for all the a values. With the use of the p_g values, the fourth terms of Eq. 16 were calculated to be as shown in Table 4. Accordingly, the relative potential energies, calculated considering only the first, second, and fourth terms of Eq. 1, are shown in the last column of Table 4. The column shows that the relative potential energies of **2**, **7**, and **8** in methanol may be higher in the order of **2**, **8**, and **7**, since $\beta_0<0$.

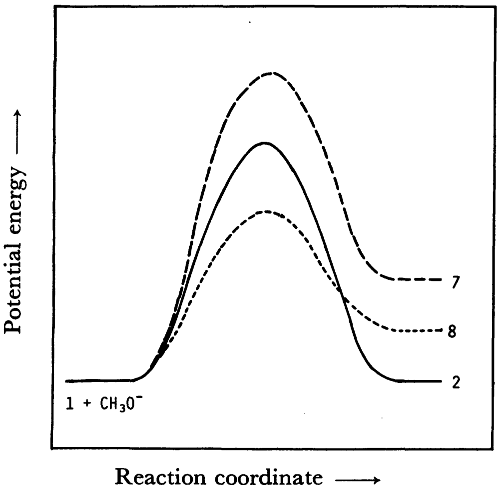


Fig. 2. Profile of potential energy curves for the formations of **2**, **7**, and **8** in methanol.

Thus, from the above discussions of the activation energies and the relative potential energies for the formations of **2**, **7**, and **8**, one may qualitatively draw the potential energy curves *vs.* an arbitrary reaction coordinate as is shown in Fig. 2. The fact that, in methanol, **5** is finally produced from **7** in spite of the activation and potential energies for **7** being highest can be explained by the irreversible reaction of **7** with methanol. Because of these energies for **7** being highest, the concentration of **7** may be small in a methanolic solution, and **5** may be irreversibly produced the most slowly. The relative permittivities of methanol and DMSO are both large. Their contributions to the activation and potential energies for the formations of **2**, **7**, and **8** do not differ considerably in the present treatments, since the contributions of the hydrogen bondings between the methanol molecules and the anions are assumed to be the same and are excluded. The potential energy curves of Fig. 2 can, therefore, probably be applied qualitatively to the case of the DMSO solvent. Thus, Fig. 2 can account for the conclusions that the formation of **2** is kinetically slower and thermodynamically more stable than that of **8**, both in methanol and in DMSO, and that the formation of **5** is the slowest in methanol and is not produced in DMSO. Bernasconi[21] found the enthalpy change of (4.2±6.7) kJ mol^{-1} for the formation of 1-methoxy-2,4,6-trinitrocyclohexadienide from 1,3,5-trinitrobenzene and the methoxide ion in methanol at 25 °C. Since the dipole moment of **1** has been estimated to be very small, as has been described above, the relationship of the relative potential energies between **2** and the system of **1** and CH_3O^- probably resembles that for the case of 1,3,5-trinitrobenzene. Accordingly, the relative potential energy of **2** is probably near that of $\mathbf{1}+CH_3O^-$. In the DMSO solution, a mixture of **2** and **8** (5%) is present at equilibrium.[6] This means that the relative potential energy of **8** is not so high as that of **2**.

Experimental

The melting points were measured by a Yanaco micromelting apparatus and were uncorrected. The IR spectra were measured as KBr disks by means of a Hitachi grating infrared spectrophotometer 215. The ^{1}H-NMR spectra were measured, with tetramethylsilane as the internal standard, on a Hitachi high-resolution NMR spectrometer, R-22 (90 MHz). The UV spectra were recorded with a Hitachi autorecording spectrophotometer 340 at room temperature.

Material. 3,5-Dinitrobenzonitrile (Aldrich) was checked for purity by means of thin-layer chromatography and was used without further purification.

Reaction of 3,5-Dinitrobenzonitrile With Sodium Methoxide in Methanol. *A)*: When 1.00 cm^3 of a CH_3ONa (1.02 mmol) solution in methanol was added to the solution prepared by dissolving 173.8 mg of **1** (0.900 mmol) in 15 cm^3 of methanol, a reddish-orange solution was immediately produced. This colored solution was acidified with an aqueous HCl solution *ca.* 2 min after the addition of CH_3ONa; a pale-orange solution was thus obtained. When the volume of the pale-orange solution was doubled with water, white crystals were precipitated; they were subsequently separated. The white crystals (mp 106.0—108.1 °C) were found to be pure by means of thin-layer chromatography. The IR spectrum of the white crystals exhibited absorption bands similar to those of the methyl ester (mp 106.0—108.0 °C) obtained by the esterification of 3,5-dinitrobenzoic acid (Kanto, G. R.). The white crystals, therefore, were identified as methyl 3,5-dinitrobenzoate; NMR(DMSO-d_6): δ=3.96 (3H, s), 8.90 (2H, d, J=2 Hz), and 9.03 ppm (1H, t, J=2 Hz); IR: 1730 and 1305 cm^{-1}.

B): When 50 mm^3 of a CH_3ONa (51.2 μmol) solution in methanol was added to the solution prepared by dissolving 1.0008 g of **1** (5.1823 mmol) in 50 cm^3 of methanol, a reddish-orange solution was immediately formed. When the colored solution was left to stand in the dark at room temperature for two days, a pale yellowish-orange solution was obtained. When the volume of the pale-colored solution was doubled with water, crystals were precipitated. The crystals were filtered off, washed three times with water, and dried. The pale yellow crystals (0.6867 g) thus isolated were found to be pure by means of thin-layer chromatography. The crystals were identified as **5**; mp 109.1 °C; UV(CH_3OH): *ca.* 230 (sh, ε 2.03×10^4), *ca.* 298 (sh, 8.3×10^2), *ca.* 310 (sh, 6.7×10^2) and *ca.* 340 nm (sh, 2.0×10^2); NMR(DMSO-d_6): δ=3.28 (1H, somewhat broad), 3.89 (3H, s), and 8.90—8.95 ppm (3H, dd); IR: 3330 and 1650 cm^{-1}. Found: C, 42.84; H, 2.95; N, 18.73%. Calcd for $C_8H_7N_3O_5$: C, 42.68; H, 3.13; N, 18.66%.

An aqueous HCl solution was added to a solution of **5** in methanol. To the resulting solution water was then added in a large quantity. Then, white crystals were precipitated and subsequently separated. The IR spectrum of the white crystals exhibited absorption bands similar to those of methyl 3,5-dinitrobenzoate.

The NMR sample prepared by adding solid CH_3ONa to a solution of **5** in DMSO-d_6 showed a spectrum characteristic of a Meisenheimer complex, *i.e.*, δ=8.43 (1H, d, J=2 Hz), 7.68 (1H, d, J=2 Hz), and 5.55 ppm (1H, s), although the sample showed a changeable spectrum for several minutes after the addition of CH_3ONa.

C): A solution of CH_3ONa (3.071 mmol) in methanol was added to a solution prepared by dissolving 0.26936 g of **1** (1.3948 mmol) in as little methanol as possible. A red solution was thus immediately formed; it was left to stand overnight in a refrigerator. After the evaporation of some of the solvent by means of a suction at room temperature, crystals precipitated; they were susequently isolated. The IR spectrum of the pale greyish crystals exhibited mainly absorption bands similar to those of **5**, besides a few weak bands due to other substances.

*Reproduction of **1** from a Red Solution of **1** and CH_3ONa in the DMSO Containing a Little Methanol.* When 1.00 cm^3 of a solution of CH_3ONa (1.024 mmol) in methanol was added to a solution prepared by dissolving 116 mg of **1** (0.601 mmol) in 3.00 cm^3 of DMSO, a red solution was immediately produced. After being shaken, the red solution was left to stand in the dark at room temperature for *ca.* 15 min. Then, two drops of an aqueous dilute solution of HCl were added to the red solution; a yellow solution resulted. When a 25-cm^3 portion of water was added to the yellow solution, white crystals were precipitated. When these crystals were filtered off, washed three times with water, and dried, pale orange crystals (72 mg) were obtained. The IR spectrum of the crystals exhibited absorption bands similar to those of **1**. A similar experiment using DMSO containing 18-crown-6 (Nisso, 1.39 mmol) also gave a reproduction of **1**.

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Appendix

Let us consider a solute molecule contained within a spherical cavity with a radius of a in an isotropic, continuous medium of a solvent with a relative permittivity of ε_r. The permittivity in the cavity is assumed to be unity. Let the origin be the center of the cavity, and let us use the polar coordinates of $\{r, \theta, \phi\}$ to express a position. Let the standard coordinate of θ be the direction of the dipole moment, $\boldsymbol{p}_g$, of the solute. One considers a collection $(\sum_{j=1}^{N} e_j)$ of N point charges for the solute molecule, and $\boldsymbol{p}_g$ is written as $\sum_{j=1}^{N} e_j r_j$.

According to Kirkwood's treatment,[12,13] the reaction potential (Φ_R) inside the cavity and the potential (Φ_O) outside the cavity can be written, respectively, as:

$$\Phi_R = \sum_{n=0}^{\infty} \frac{(n+1)(1-\varepsilon_r)}{(n+1)\varepsilon_r+n} \times \frac{1}{a^{2n+1}} \times \sum_{j=1}^{N} e_j r_j^n r^n \mathrm{P}_n(\cos\theta_{jr}), \tag{i}$$

and:

$$\Phi_O = \sum_{n=0}^{\infty} \frac{(2n+1)}{(n+1)\varepsilon_r+n} \times \frac{1}{r^{n+1}} \times \sum_{j=1}^{N} e_j r_j^n \mathrm{P}_n(\cos\theta_{jr}), \tag{ii}$$

where P_n $(\cos\theta_{jr})$ is a simple Legendre polynomial and θ_{jr} is the difference in θ between the positions of $\{r, \theta, \phi\}$ and $\{r_j, \theta_j, \phi_j\}$. Neglecting terms higher than $n=1$, one reduces Φ_R and Φ_O to:

$$\Phi_{\mathrm{R}}(n=1) = \frac{(1-\varepsilon_{\mathrm{r}})}{\varepsilon_{\mathrm{r}}} \times \frac{1}{a}\left(\sum_{j=1}^{N} e_j\right) + \frac{2(1-\varepsilon_{\mathrm{r}})}{2\varepsilon_{\mathrm{r}}+1} \times \frac{1}{a^3}\sum_{j=1}^{N} e_j r_j r \cos\theta_{jr}, \tag{iii}$$

and:

$$\Phi_{\mathrm{O}}(n=1) = \frac{1}{\varepsilon_{\mathrm{r}}} \times \frac{1}{r}\left(\sum_{j=1}^{N} e_j\right) + \frac{3}{2\varepsilon_{\mathrm{r}}+1} \times \frac{1}{r^2}\sum_{j=1}^{N} e_j r_j \cos\theta_{jr}, \tag{iv}$$

respectively. From Eq. iii, one immediately obtains the reaction potential, $\Phi_{\mathrm{R}}(0)$, at the origin as:

$$\Phi_{\mathrm{R}}(0) = \frac{(1-\varepsilon_{\mathrm{r}})}{\varepsilon_{\mathrm{r}}} \times \frac{1}{a}\left(\sum_{j=1}^{N} e_j\right). \tag{v}$$

The electric field, E_r, outside the cavity is obtained by $\boldsymbol{E}_r = -\partial\Phi_{\mathrm{O}}\,(n=1)/\partial r$ in the direction of $\boldsymbol{r}$. The polarization charge, P_a, induced per unit of area over the cavity is given by putting $r=a$ into the equation of $P_r = \{(\varepsilon_{\mathrm{r}}-1)/4\pi\}\cdot|\boldsymbol{E}_r|$. The charge induced on the infinitesimal area of the cavity surface contained in the solid angle between θ_{jr} and $(\theta_{jr} + \mathrm{d}\theta_{jr})$ is given by $2\pi a^2 P_a \sin\theta_{jr}\,\mathrm{d}\theta_{jr}$, which produces an electric field of $2\pi P_a \sin\theta_{jr}\cos\theta_{jr}\,\mathrm{d}\theta_{jr}$ at the origin in the direction of $\boldsymbol{p}_{\mathrm{g}}$. Then, the reaction field, $\boldsymbol{R}$, parallel to $\boldsymbol{p}_{\mathrm{g}}$ at the point of origin is obtained as follows:

$$\begin{aligned}\boldsymbol{R} &= 2\pi\int_0^{\pi} P_a \sin\theta_{jr}\cos\theta_{jr}\,\mathrm{d}\theta_{jr} \\ &= \frac{(\varepsilon_{\mathrm{r}}-1)}{2\varepsilon_{\mathrm{r}}a^2} \times \left(\sum_{j=1}^{N} e_j\right)\int_0^{\pi}\sin\theta_{jr}\cos\theta_{jr}\,\mathrm{d}\theta_{jr}, \\ &\quad + \frac{3(\varepsilon_{\mathrm{r}}-1)\boldsymbol{p}_{\mathrm{g}}}{(2\varepsilon_{\mathrm{r}}+1)a^3}\int_0^{\pi}\sin\theta_{jr}\cos^2\theta_{jr}\,\mathrm{d}\theta_{jr}, \\ &= \frac{\varepsilon_{\mathrm{r}}-1}{2\varepsilon_{\mathrm{r}}+1} \times \frac{2\boldsymbol{p}_{\mathrm{g}}}{a^3}.\end{aligned} \tag{vi}$$

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