D. Thermal Decomposition of the Sodium Salt of 4-Hydroxy-4-methylvaleric Acid γ-Lactone Tosylhydrazone (3d). The condensable portion of the pyrolysate obtained from **3d** gave two components on elution from column A. The first component, formed in 11% yield, was identified as 2,3-dihydro-2,2-dimethylfuran by comparison of its ir and nmr spectra with those obtained from authentic[21] material: ir (CCl$_4$) 1615, 1110, 1050, 685 cm^{-1}; nmr (60 MHz, CCl$_4$) δ 1.22 (s, 6 H), 2.28 (t, 2 H), 4.57 (q, 1 H), 6.02 (q, 1 H). The second component, formed in 28% yield, was identified as 2,2-dimethylcyclobutanone by comparison of its ir and nmr spectra with those obtained from authentic[22] material.

The gaseous portion of the pyrolysate contained a 26% yield of 2-methylpropene and an 11% yield of 1,1-dimethylcyclopropane, both identical with authentic samples by analytical vpc and gcms using column C.

E. Thermal Decomposition of the Sodium Salt of 5-Hydroxyvaleric Acid δ-Lactone Tosylhydrazone (4d). The condensable portion of the pyrolysate obtained from **4d** gave three components on elution from column B. The first component, formed in 17% yield, was identified as 3,4-dihydro-2*H*-pyran by comparison of its ir and nmr spectra with those obtained from authentic commercially available material: nmr (220 MHz, CCl$_4$) δ 1.84 (m, 2 H), 1.98 (m, 2 H), 3.91 (m, 2 H), 4.57 (m, 1 H), 6.28 (m, 1 H). The second component, formed in 6% yield, was identified as 4-pentenal by comparison of its ir and nmr spectra with those obtained from authentic[23] material: ir (CCl$_4$) 1730, 1640, 985, 910 cm^{-1}; nmr (220 MHz, CCl$_4$) δ 2.36 (m, 2 H), 2.48 (m, 2 H), 5.00 (m, 2 H), 5.80 (m, 1 H), 9.70 (s, 1 H). The third component, formed in 61% yield, was identified as cyclopentanone by comparison of its ir and nmr spectra with those obtained from authentic material.

The gaseous portion of the pyrolysate contained virtually no ethylene or cyclobutane, the upper limit for either of these compounds being established as 0.10% by analytical vpc using column C.

F. Thermal Decomposition of the Sodium Salt of 6-Hydroxyhexanoic Acid ϵ-Lactone Tosylhydrazone (5d). The condensable portion of the pyrolysate obtained from **5d** gave three components on elution from column B. The first component, formed in 11% yield, was identified as 2,3,4,5-tetrahydrooxepin by comparison of its ir and nmr spectra with published[24] values: nmr (220 MHz, CCl$_4$) δ 1.65 (m, 2 H), 1.74 (m, 2 H), 2.09 (m, 2 H), 3.83 (t, J = 5.5 Hz, 2 H), 4.60 (d of t, J_1 = 7.0 Hz, J_2 = 5.5 Hz, 1 H), 6.15 (d of t, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 1 H). The second component, formed in 16% yield, was identified as 5-hexenal by comparison of its ir and nmr spectra with those obtained from authentic[25] material: ir (CCl$_4$) 1730, 1640, 985, 910 cm^{-1}; nmr (220 MHz, CCl$_4$) δ 1.71 (m, 2 H), 2.09 (m, 2 H), 2.37 (t, J = 7 Hz, 2 H), 4.98 (m, 2 H), 5.72 (m, 1 H), 9.74 (s, 1 H). The third component, formed in 60% yield, was identified as cyclohexanone by comparison of its ir and nmr spectra with those obtained from authentic material.

The gaseous portion of the pyrolysate contained a 0.13% yield of cyclopentane, which was identical with an authentic sample by analytical vpc using column C, and gcms using column D.

2-Imino-5,5-dimethyltetrahydrofuran Hydrobromide (3b). This salt was prepared from isocaproamide[26] (7) in 55% yield by the procedure described[12] in detail for related compounds: mp 208–210° dec from acetone; ir (KBr) 1716 (s), 1455 (m), 1098 (m), 775 (m) cm^{-1}.

Anal. Calcd for C$_6$H$_{12}$NOBr: C, 37.12; H, 6.24; N, 7.22. Found: C, 37.11; H, 6.37; N, 7.19.

Hydrolysis of 3b. A mixture of 150 mg of **3b**, 1.0 ml of 0.5 M aqueous hydrochloric acid, and 3 ml of ether was stirred at room temperature overnight and then worked up with more water and ether. The ether extracts were dried over sodium sulfate and yielded 60 mg (68%) of isocaprolactone (**10**), which was identified by comparison of its vpc retention time and ir spectrum with an authentic sample.[13]

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(21) The authentic sample was prepared by Mr. David K. Herron following reported procedures: J. Colonge and P. Garnier, *Bull. Soc. Chim. Fr.*, 432 (1948); D. A. Barr and J. B. Rose, *J. Chem. Soc.*, 3766 (1954).

(22) W. C. Agosta and D. K. Herron, *J. Org. Chem.*, **34**, 2782 (1969).

(23) The authentic sample was prepared from 4-penten-1-ol by the method used for 5-hexenal below.

(24) D. R. Larkin, *J. Org. Chem.*, **30**, 335 (1965).

(25) W. C. Agosta, D. K. Herron, and W. W. Lowrance, Jr., *Tetrahedron Lett.*, 4521 (1969).

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Kinetics of the Reaction of 1,3-Dinitrobenzene with Methoxide Ion in Methanol Solution

I. R. Bellobono,*[1] A. Gamba, G. Sala, and M. Tampieri

Contribution from the Istituto di Chimica Fisica dell'Università di Milano, 20133 Milan, Italy. *Received November 29, 1971*

Abstract: In the redox reaction of 1,3-dinitrobenzene with methoxide ion to yield *trans*-3,3′-dinitroazoxybenzene, the presence of 1,3-dinitrobenzene radical anion was detected both by electron paramagnetic resonance and electronic spectroscopy: its role as reaction intermediate was established. Kinetic parameters of this reaction were determined at 40–90° in CH$_3$OH solutions containing 0.14–4.90 M CH$_3$O$^-$. Kinetic measurements show that the rate of formation of the radical anion is equal to that of disappearance of 1,3-dinitrobenzene and to that of formation of another intermediate, which on the basis of spectroscopic evidence can be identified as a species closely related to *m*-nitronitrosobenzene. This latter species finally reacts to give the product. Hyperfine couplings for radical anion produced in dimethyl sulfoxide solution containing 0, 2, and 20 vol % CH$_3$OH show extensive solvation of nitro group by CH$_3$OH.

The reduction of nitro groups in nitroaromatics by alkoxide ions to yield the corresponding azoxy derivatives, with simultaneous oxidation of the base, is solely confined to mononitro- and *m*-dinitrobenzenes, whereas nucleophilic aromatic substitutions of nitro group are kinetically preferred by other dinitro- and

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[1] Present address: Istituto Chimico dell'Università di Roma; 00185 Rome, Italy.

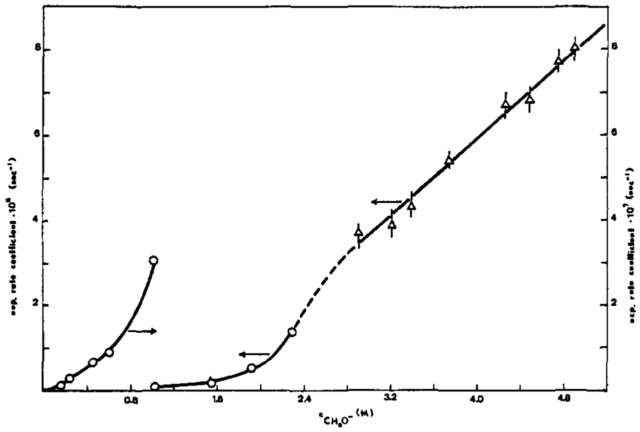

Figure 1. Experimental pseudo-first-order rate coefficients for the reaction of 1,3-dinitrobenzene with methoxide ion in methanol solution at 40°, as a function of sodium methoxide concentration.

trinitrocompounds. The redox reaction has been known for a long time[2] and more recently has attracted growing interest both in preparative work[3,4] and in technological applications.

Very little, however, is known about the course of the reaction, except the stoichiometry and kinetics of the simplest case of reduction of nitrobenzene by sodium methoxide in methanol[5,6] and the fact that the oxygen of the nitro group is (partly) transferred to the base.[7]

In the course of our studies on the reactivity of polynitroaromatics with bases, we have hitherto considered addition complex formation,[8] as well as nucleophilic substitution[9] and hydrogen exchange reactions.[10] The behavior of 1,3-dinitrobenzene (*m*-DNB) toward base addition is particularly interesting for the fact that two addition complexes are possible,[10a] whether the σ bonding takes place at the 4- or at the 2-carbon atom of the benzene ring. The first kind of complex, which results from addition of nitrogen bases or of bulky alkoxides, such as *tert*-butoxide in dimethyl sulfoxide solution, has been well identified by its nmr spectrum.[11,12] It also shows a typical violet color corresponding to an electronic absorption spectrum with two maxima at 360 and 560 nm in ethylenediamine solution (molar absorptivities 11,900 and 25,400 M^{-1} cm^{-1}, respectively).[8a,8b,10a] In aqueous ethylenediamine solution the 1,3-dinitro-4-ethylenediaminocyclohexa-2,5-dienate is slowly converted into the isomer 1,3-dinitro-2-ethylenediaminocyclohexa-3,5-dienate.[8] This latter type of brown-colored complex, the electronic spectrum of which presents a single maximum at 398 nm (molar absorptivity 16,000 M^{-1} cm^{-1}) in ethylenediamine solution, could be directly isolated and characterized by its nmr absorption[13] when the addition reaction was carried out in methanol solution with sodium methoxide[10a] at a sufficiently low temperature (about 5°), in order to minimize the concurrent reduction of nitro group.

The present paper mainly concerns kinetics of the chemical reduction of nitro group in *m*-DNB. The preparation of *trans*-3,3,′-dinitroazoxybenzene by this latter reaction had been early reported by Michler,[14] by Klinger and Pitschke,[15] and by others[16-18] The electrochemical reduction of *m*-DNB to 3-nitrophenylhydroxylamine has been recently studied in liquid ammonia[19a] and in dimethyl sulfoxide solution.[19b] The first reduction step corresponded to the formation of the 1,3-dinitrobenzene radical anion (*m*-DNB·$^-$), which reacts with a proton donor to give the product. The electrolytic or alkali-metal reduction of *m*-DNB to *m*-DNB·$^-$ has been thoroughly studied.[20,21] The presence of *m*-DNB·$^-$ was also detected in the interaction between alkoxides, such as potassium *tert*-butoxide, and *m*-DNB.[22]

Results and Discussion

The reaction between *m*-DNB and methoxide ion in methanol solution containing 0.15–0.50 *M* of both reagents obeyed the following overall stoichiometry, up to a conversion degree of about 94% at 64°.

$$4m\text{-}(NO_2)C_6H_4NO_2 + 3CH_3O^- \longrightarrow 2m\text{-}(NO_2)C_6H_4N{=}N(O)C_6H_4(NO_2)\text{-}m + 3HCOO^- + 3H_2O \quad (1)$$

This has been established by titration of methoxide, chemical and spectrophotometric analysis of *m*-DNB and product, as well as by gas chromatographic detection of formic acid.

Kinetics of reaction 1 was examined at 40–95°. It resulted first order both in *m*-DNB and in methoxide ion. In excess of the latter, however, pseudo-first-order rate coefficients were not a linear function of methoxide ion concentration in the range 0.14–2.3 *M* CH_3O^-, as can be observed in Figure 1. In this concentration range the transformation of *m*-DNB into *trans*-3,3′-dinitroazoxybenzene was followed by spectrophotometric analysis, without any evidence of formation of other intermediates or products, with the exception of minor amounts (<12% as estimated spectrophotometrically) of sodium 1,3-dinitro-2-methoxycyclohexa-3,5-dienate. A similar situation was found for other reactions involving methoxide ion in methanol solution, such as nucleophilic substitution of nitro group[9] and hydrogen exchange.[10b,c] In these, as well

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[3] W. Tadros, M. S. Ishak, and E. Bassili, *J. Chem. Soc.*, 627 (1959).

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[8] (a) G. Favini and I. R. Bellobono, *Ann. Chim. (Rome)*, **50**, 825 (1960); (b) *ibid.*, **51**, 841 (1961); (c) I. R. Bellobono and G. Favini, *ibid.*, **57**, 325 (1967).

[9] (a) I. R. Bellobono, *Ric. Sci.*, **39**, 358, 365 (1969); (b) I. R. Bellobono and G. M. Sabbadini, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, **48**, 226 (1970).

[10] (a) I. R. Bellobono, *Ric. Sci.*, **39**, 170 (1969); (b) I. R. Bellobono and M. Tampieri, *Ann. Chim. (Rome)*, **60**, 466 (1970); (c) I. R. Bellobono and G. Sala, *J. Chem. Soc., Perkin Trans. 2*, **68**, 169 (1972).

[11] C. A. Fyfe and R. Foster, *Chem. Commun.*, 1219 (1967).

[12] Chemical shifts (τ, ppm) were measured with tetramethylsilane as internal standard: C-2, 1.68; C-5, 4.62; C-6, 3.39; C-4, 5.83 (acetone–dimethyl sulfoxide 1:1 as solvent).

[13] Chemical shifts (as in preceding footnote) were C-2, 3.4; C-4, C-5, and C-6, 1.7 (methanol solution).

[14] W. Michler, *Ber.*, **6**, 746 (1873).

[15] H. Klinger and R. Pitschke, *ibid.*, **18**, 2551 (1885).

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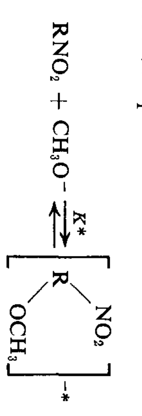
[22] (a) G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4153 (1962); (b) *ibid.*, **86**, 1807 (1964).

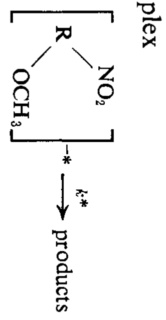
as in the present case, when reaction kinetics were carried out in pseudo-first-order conditions and no linear correlation existed between the relative kinetic coefficients and concentration of methoxide ions, consistent values of second-order rate constants were obtained by expressing the rate r equation in terms of activities of methoxide ions.

$$r = k^*K^*c_{RNO_2}c_{CH_3O^-}\frac{f_{RNO_2}f_{CH_3O^-}}{f_*} = kc_{RNO_2}c_{CH_3O^-}\frac{f_{CH_3O^-}}{f_\pm} = kc_{RNO_2}a_{CH_3O^-} \qquad (2)$$

where c are concentrations, f are activity coefficients of RNO_2, CH_3O^-, and activated complex (*), respectively, K^* is the equilibrium constant between reagents and activated complex



k^* is the first-order decomposition constant of the activated complex



and $a_{CH_3O^-}$ is the "kinetic activity" of methoxide ion, as expressed by eq 2. The latter was suitably evaluated by some approximations such as considering the activity coefficient of the activated complex f_* equal to $f_\pm$, the mean ionic activity coefficient of the acid-base couple of indicators used to measure the H_M acidity function in methanol solution of sodium methoxide[23,24]

$$\log c_{CH_3O^-}f_{CH_3O^-} = H_M - pK_S + \log f_\pm \qquad (3)$$

where K_S is the autoprotolysis constant of methanol.

Experimental pseudo-first-order rate coefficients k_1 and second-order rate constants $k(k = k_1/a_{CH_3O^-})$ calculated by the above procedure in solutions containing 0.4–2.3 M CH_3O^- are reported in Table I.

Activation parameters obtained by an Arrhenius plot of k data were activation energy $\Delta E^{\ddagger} = 24.5 \pm 0.4$ kcal/mol and preexponential factor (A in M^{-1} sec^{-1}) $\log A = 10.17 \pm 0.15$.

When the concentration of methoxide ion was increased to 3–5 M CH_3O^- the apparent course of the reaction, as it could be followed spectrophotometrically, changed. The disappearance of *m*-DNB (maximum absorption at 235 nm in methanol solution) became faster and faster and the formation of two intermediate species was detected. An intermediate species I, exhibiting an absorption band at about 275 nm, in the reaction mixture, was observed, the concentration of which passed through a maximum and then more slowly decreased, evolving toward the product (3,3′-dinitroazoxybenzene). The appearance of the typical

Table I. Rate Coefficients for the Reaction of 1,3-Dinitrobenzene with Methoxide Ion in Methanol Solution at Various Temperatures and Sodium Methoxide Concentrations

40.00°, c_{CH_3ONa}, M	0.142	0.211	0.442	0.571	0.998	1.52	1.91	2.28	2.89	3.20
k_1, sec^{-1} × 10^7	0.16 ± 0.04	0.26 ± 0.06	0.61 ± 0.08	0.88 ± 0.09	3.01 ± 0.13	16.5 ± 2.9	48.6 ± 5.3	131 ± 15	345 ± 32[a]	866 ± 64[a]
k, M^{-1} sec^{-1} × 10^7					1.26 ± 0.14					
c_{CH_3ONa}, M	2.89	3.20	3.40	3.75	4.25	4.58	4.75	4.90		
k_2, sec^{-1} × 10^4	0.37 ± 0.03	0.85 ± 0.05	1.75 ± 0.12		24.8 ± 1.6					
k_3, sec^{-1} × 10^5	3.67 ± 0.28	3.98 ± 0.31	4.59 ± 0.25	5.33 ± 0.26	6.65 ± 0.25	6.75 ± 0.22	7.62 ± 0.28	7.93 ± 0.30		
k_4, sec^{-1} × 10^4	0.38 ± 0.04	0.88 ± 0.03	1.65 ± 0.10							
k_5, sec^{-1} × 10^6	8.05 ± 0.78	7.23 ± 0.65	8.81 ± 0.90							
54.80°, c_{CH_3ONa}, M	1.51	1.71	1.83							
k_1, sec^{-1} × 10^6	6.53 ± 0.24	12.5 ± 0.75	19.3 ± 1.4							
k, M^{-1} sec^{-1} × 10^7		6.31 ± 0.28								
65.15°, c_{CH_3ONa}, M	0.985	1.070	1.206							
k_1, sec^{-1} × 10^6	5.74 ± 0.36	7.32 ± 0.28	9.47 ± 0.38							
k_1, M^{-1} sec^{-1} × 10^6		2.40 ± 0.13								
80.15°, c_{CH_3ONa}, M	0.596	0.693	0.738	1.07	1.21	1.33				
k_1, sec^{-1} × 10^5	1.39 ± 0.05	2.04 ± 0.07	2.88 ± 0.09	2.95 ± 0.08	4.39 ± 0.11	5.83 ± 0.15				
k_1, M^{-1} sec^{-1} × 10^5				1.02 ± 0.06						
90.70°, c_{CH_3ONa}, M	0.674	0.707	0.784	1.05	1.15	1.29				
k_1, sec^{-1} × 10^6	3.01 ± 0.06	3.79 ± 0.05	4.58 ± 0.06	6.72 ± 0.09	9.53 ± 0.23	1.50 ± 0.07				
k, M^{-1} sec^{-1} × 10^5				2.80 ± 0.12						
95.20°, c_{CH_3ONa}, M	1.30	1.38	1.53							
k_1, sec^{-1} × 10^4	2.54 ± 0.08	3.83 ± 0.09	4.78 ± 0.11							
k, M^{-1} sec^{-1} × 10^5		4.66 ± 0.19								

[a] Evaluated only by the rate of disappearance of *m*-DNB.

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spectrum of this latter was always the last step of the reaction. The pseudo-first-order rate constants for the transformation I $\rightarrow$ 3,3′-dinitroazoxybenzene varied linearly with methoxide ion concentration up to the highest limit investigated, as is shown in Figure 1. The rate constant (k_2) for the formation of I could be evaluated only in the upper range of methoxide concentration, where the concentration maximum of I was clearly visible; it was calculated from the time $t_{\max}$ at which I reached its maximum concentration and the pseudo-first-order rate constant k_3 for the transformation I $\rightarrow$ 3,3′-dinitroazoxybenzene, following the relationship of consecutive first-order reactions

$$t_{\max} = (\ln k_3/k_2)/(k_3 - k_2) \qquad (4)$$

In a narrow concentration range, 2.9–3.4 M CH_3O^-, and with a *m*-DNB concentration 10 times that used during the spectrophotometric analysis in the ultraviolet region for the detection of species I, the formation of another intermediate species II was also observed, which exhibited an absorption band at 495 nm. Concentration of this species passed through a maximum and then decreased to give rise to species I, which in turn decomposed into 3,3′-dinitroazoxybenzene, as the main product and into a minor quantity (about 12–18%) of sodium 1,3-dinitro-2-methoxycyclohexa-3,5-dienate (absorbing at 395 nm). Rate of decrease of species II was followed spectrophotometrically at 480–500 nm, a wavelength range where only this species contributed to absorption. The relative pseudo-first-order kinetic coefficients k_5 are reported in Table I. Rate coefficients k_4 for the formation of II were calculated, following relationship 4 of consecutive first-order reactions, from the time $t_{\max}$ at which II reached its maximum absorption and the rate constant for its decomposition. From experimental data of Table I some conclusions may be drawn. When the concentration of methoxide ion is less than 2.89 M the rate of formation of 3,3′-dinitroazoxybenzene is equal to that of disappearance of *m*-DNB. In contrast, when concentration of methoxide ion exceeds 2.89 M, it clearly appears that the rate coefficient k_2 for production of intermediate species I is equal to that for disappearance of *m*-DNB (k_1). Also the rate coefficient for production of intermediate species II (k_4) equals that of disappearance of *m*-DNB. The latter, however, does not represent the rate coefficient (k_3) for production of 3,3′-dinitroazoxybenzene (from intermediate species I), which results from a slower process. The concentration of 2.89 M CH_3O^- is thus a critical value above which the rate-determining process becomes the decomposition of intermediate species I. As the rate coefficient for disappearance of species II (k_5) is greater than that of transformation of species I into 3,3′-dinitroazoxybenzene, it must be inferred that species II is the first intermediate of the reaction between *m*-DNB and CH_3O^-, and that k_5 concerns the conversion of II into I and into minor quantities of the addition compound sodium 1,3-dinitro-2-methoxycyclohexa-3,5-dienate. For this reason, the detection of species II was possible only in a limited concentration range around the critical value (2.89 M CH_3O^-), where all the rate coefficients k_1 (disappearance of *m*-DNB and formation of product), k_2 (formation of species I), k_3 (decomposition of species I into product), and k_4 (formation of species II) had nearly the same value at 40° (3.5–3.8 $\times$ 10^{-5} sec^{-1}), and where the rate of formation of species II had the same order of magnitude as that of its decomposition.

It was impossible to attribute absorption of species II at 495 nm to any addition compound. The only possibility would have been to regard the 495-nm absorption in methanol solution as due to a 65-nm hypsochromic displacement of the 560-nm band exhibited by 1,3-dinitrocyclohexa-2,5-dienates in various solvents ranging from dimethyl sulfoxide to ethylenediamine. Aside from any consideration on the magnitude of solvent shifts of optical spectra, this was ruled out by the fact that dilution with methanol of a preformed "violet" complex in dimethyl sulfoxide solution did not appreciably shift the frequency of the 560-nm band of this complex.

The possibility of species II being the radical anion intermediate *m*-DNB$\cdot^-$ was investigated. While the visible spectroscopy of the one-electron reduction product of mononitrobenzene has been extensively studied,[25–28] the electronic spectrum of *m*-DNB$\cdot^-$ does not appear to have been measured. The spectrum of electrolytically generated *m*-DNB$\cdot^-$ in dimethyl sulfoxide solution was recorded immediately after the preparation of the solution *in vacuo*.[29] It showed a single maximum at 520 nm in dimethyl sulfoxide. This maximum was shifted to 495 nm in methanol solution. The formation of *m*-DNB$\cdot^-$ was furthermore detected by electron spin resonance in a 0.02 M solution of *m*-DNB in dimethyl sulfoxide, containing 2 and 20 vol % CH_3OH with 0.01 M CH_3ONa at 25°. The hyperfine coupling constants are reported in Table II together with those of electrolytically generated *m*-DNB$\cdot^-$ in dimethyl sulfoxide for reference purpose.

Table II. Hyperfine Coupling Constants (in Gauss) of 1,3-Dinitrobenzene Radical Anion

	a_N	a_{H-2}	a_{H-4}	a_{H-5}	a_{H-6}
A[a]	4.13	2.97	4.13	1.14	4.13
B[b]	9.07	4.05	3.01	1.01	4.05
C[b]	11.16	3.95	3.30	1.06	3.95

[a] 0.02 M electrolytically generated *m*-DNB$\cdot^-$ in dimethyl sulfoxide solution. [b] 0.02 M *m*-DNB, 0.01 M CH_3ONa in dimethyl sulfoxide solution containing 2(B) or 20(C) vol % methanol.

The addition of dimethyl sulfoxide was necessary to record esr spectra in order to slow down decomposition of *m*-DNB$\cdot^-$ in pure methanol and obtain a satisfactory resolution. Owing to interaction with the solvent the nitrogen $M_I = \pm 1$ states broadened as the concentration of methanol in dimethyl sulfoxide increased and a line width alternated spectrum was observed for chemically produced *m*-DNB$\cdot^-$ in methanol–dimethyl sulfoxide solution (*cf.* spectra B and C in Table II): a situation similar to that reported for this same radical anion in dimethylformamide–ethanol

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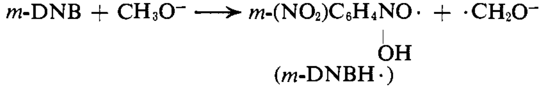
(29) After some time, also a base addition complex was formed in dimethyl sulfoxide, the "violet" compound absorbing at about 570 nm, probably due to the addition of dimethylsulfinyl anion to the 4 position of the *m*-DNB ring.

solution.[30,31] For this reason B and C spectra (*cf.* Table II) of radical anion indicate interaction with only one nitrogen. Since it is evident from esr data that the ground state of m-DNB$\cdot^-$ is strongly solvated by methanol in dimethyl sulfoxide, the excited state will be less solvated. This fact may interpret the blue shift of the optical spectrum from dimethyl sulfoxide to methanol, in keeping with current theories on the influence of solvent.[32,33]

All the above evidence points toward the identification of species II as m-DNB$\cdot^-$ and leads to the conclusion that m-DNB$\cdot^-$ acts as an intermediate in the chemical reduction mechanism of m-DNB by CH_3O^- in methanol solution.

As to species I, its maximum absorption, which falls in the same wavelength range as that of m-nitronitrosobenzene in methanol solution,[34] and the linear dependence of its decomposition rate on methoxide ion concentration substantiate the hypothesis that this intermediate could be identified as a species closely related to m-nitronitrosobenzene.

A likely pathway, which is consistent with all the preceding considerations, may be the following



$$m\text{-DNB} + CH_3O^- \xrightarrow{k_1} \underset{(m\text{-DNBH}\cdot)}{m\text{-}(NO_2)C_6H_4\underset{\overset{|}{OH}}{N}O\cdot} + \cdot CH_2O^- \qquad (5)$$

$$m\text{-DNBH}\cdot + CH_3O^- \overset{\text{fast}}{\rightleftarrows} m\text{-DNB}\cdot^- + CH_3OH \qquad (6)$$

$$m\text{-DNB} + \cdot CH_2O^- \xrightarrow{\text{fast}} m\text{-DNB}\cdot^- + CH_2O \qquad (7)$$

$$2m\text{-DNB}\cdot^- + 2CH_3OH \xrightarrow{k_5} m\text{-DNB} + m\text{-}(NO_2)C_6H_4NO + 2CH_3O^- + H_2O \qquad (8)$$

$$m\text{-}(NO_2)C_6H_4NO + CH_3O^- \xrightarrow{\text{fast}} m\text{-}(NO_2)C_6H_4NOH\cdot + \cdot CH_2O^- \qquad (9)$$

$$m\text{-}(NO_2)C_6H_4NOH\cdot + CH_3O^- \overset{\text{fast}}{\rightleftarrows} m\text{-}(NO_2)C_6H_4NO\cdot^- + CH_3OH \qquad (10)$$

$$m\text{-}(NO_2)C_6H_4NO + \cdot CH_2O^- \xrightarrow{\text{fast}} m\text{-}(NO_2)C_6H_4NO\cdot^- + CH_2O \qquad (11)$$

$$2m\text{-}(NO_2)C_6H_4NO\cdot^- \rightleftarrows m\text{-}(NO_2)C_6H_4N(O)^-\text{—}N(O)^-C_6H_4(NO_2)\text{-}m \qquad (12)$$

$$m\text{-}(NO_2)C_6H_4N(O)^-\text{—}N(O)^-C_6H_4(NO_2)\text{-}m + CH_3OH \rightleftarrows m\text{-}(NO_2)C_6H_4N(OH)\text{—}N(O)^-C_6H_4(NO_2)\text{-}m + CH_3O^- \qquad (13)$$

$$m\text{-}(NO_2)C_6H_4N(OH)\text{—}N(O)^-C_6H_4(NO_2)\text{-}m + CH_3OH \longrightarrow m\text{-}(NO_2)C_6H_4N{=}N(O)C_6H_4(NO_2)\text{-}m + CH_3O^- + H_2O \qquad (14)$$

where k_1 and k_5 have the same significance as in Table I, whereas k_3, the experimental rate coefficient for the disappearance of species I, is probably a composite constant, which takes into account preequilibria 10, 12, and 13.

When a factor of 4 is applied to reactions 5–8, a factor of 2 to reactions 9–14, and disproportionation[35] of excess CH_2O is considered, the reaction scheme 5–14 yields the overall stoichiometry of reaction 1.

The role of formaldehyde radical anion in reductions which occur in alkaline methanol has been discussed by Bunnett and Wamser.[36]

Reaction 6 can be viewed as an acid–base equilibrium, the position of which is not relevant to this mechanism. However, the fact that m-DNB$\cdot^-$ was the only radical species detected experimentally suggests that equilibrium 6 is shifted to the right. Reaction 7 is an electron-transfer process, which may be expected to occur with considerable ease. The alternative release of an electron from $\cdot CH_2O^-$ to the solvent, forming CH_2O and solvated electron, followed by reaction of the latter with m-DNB to yield m-DNB$\cdot^-$, seems unlikely on the basis of energetic considerations. The dismutation 8 of m-DNB$\cdot^-$ in the presence of proton donors is a well-documented reaction.[19] Experimental data suggest a unimolecular rate-determining process with respect to the radical anion, both when the reaction sequence leads to m-nitrophenylhydroxylamine as the final product[19b] or to the azoxy derivative as in the present case. However, the data thus far cannot definitely establish a detailed mechanism for step 8.

Finally the transformation of nitrosobenzene, *via* its radical anion, into the azoxy derivative has been studied in detail by Russell and Geels[37] and found to be a relatively fast reaction in alcoholic solution. The reaction sequence 9–14 stems from the mechanism proposed by these authors. Incidentally, we observed that m-nitronitrosobenzene, in absence of oxygen, transforms rapidly in methanol solution containing about 1 M CH_3ONa into the azoxy derivative, while this reaction is slow in the more alkaline solutions (>3 M CH_3ONa). In these latter media, the same species I was detected, the formation and decomposition of which was followed during the reaction between m-DNB and methoxide ion. Kinetic examinations starting from m-nitronitrosobenzene are in progress: preliminary results indicate that the formation of species I from m-nitronitrosobenzene is a fast process, followed by the slower transformation of I into the azoxy compound. A thorough study of this kinetics, particularly as a function of temperature and methoxide concentration, should give more definite information about this stage of the reaction. A mechanism based on a purely thermal decomposition (disproportionation) of the nitroso intermediate, obeying the stoichiometry

$$3m\text{-}(NO_2)C_6H_4NO \longrightarrow m\text{-}(NO_2)C_6H_4N{=}N(O)C_6H_4(NO_2)\text{-}m + m\text{-}(NO_2)C_6H_4NO_2 \qquad (15)$$

seems less probable under the experimental conditions used, owing to the observed dependence of the decomposition rate of m-nitronitrosobenzene on methoxide ion concentration.

Experimental Section

Materials. Reagent grade 1,3-dinitrobenzene was purified by recrystallization from methanol (mp 90°). Methanol was dehydrated by distillation in the presence of magnesium methoxide;

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2-methyl-2-propanol in the presence of potassium *tert*-butoxide. Dimethyl sulfoxide was dehydrated by passage over molecular sieves, followed by distillation in the presence of dimethylsulfinylsodium. Stock solutions of sodium methoxide (about 5.5 M) in methanol were prepared by dipping freshly cut pieces of sodium into methanol for about 30 sec, this operation being repeated twice, each time in a new solvent, and then transferring them to the purified solvent until dissolution was completed. The slightly cloudy solution was filtered through sintered glass filters and titrated with aqueous standardized HCl. All manipulations and transfers were done in a dry nitrogen atmosphere.

Stereochemical identification of the product, *trans*-3,3′-dinitroazoxybenzene (mp 149.5°, molar absorptivity (M^{-1} cm^{-1}) at 316 nm 15,800, at 256 nm 23,200 in methanol solution), was made on the basis of dipole moment (4.36 ±0.02 D in benzene solution at 25°) comparison with the literature values[38] of *cis*-(4.7 D) and *trans*-azoxybenzene (1.7 D) and by means of vector composition analysis.

Kinetic Procedure. Solutions ((1.24–2.4) × 10^{-4} M) of 1,3-dinitrobenzene in anhydrous methanol were prepared and mixed (1:1 volume ratio) with 0.28–4.6 M CH_3ONa in CH_3OH, obtained by appropriately diluting the stock solution of alkoxide. Aliquots of the reaction solution were placed in nitrogen-filled tubes equipped with pressure plugs. The reaction was initiated by immersing the tubes in a constant temperature bath and was stopped, when desired, by quenching. Reaction tubes were removed at regular intervals for spectrophotometric analysis. "Infinity time" absorption was measured experimentally. Kinetic runs at 40° and those in the highly concentrated methoxide solutions (>2.3 M) were followed directly in the thermostated spectrophotometric cell. Concentration of substrate was (5.0–6.2) × 10^{-5} M for analysis in the ultraviolet region and was increased by a factor of 10 when operating in the visible range of the spectrum. Pseudo-first-order equations were employed to obtain kinetic coefficients. The base concentrations shown in Table I are corrected for solution expansion by multiplying concentrations at room temperature by the ratio of the density of methanol[39] at the reaction temperature to that at room temperature.

The estimated errors determined by straightforward methods are reported as standard deviations for rate coefficients and probable errors for kinetic parameters.

Electron Spin Resonance Measurements. The instrument used to record esr spectra was a Varian[40] V-4502-11X band spectrometer with a 100-KHz magnetic field modulation. Electrochemical generation of 1,3-dinitrobenzene radical anion was effected in a 0.02 M solution of 1,3-dinitrobenzene in dimethyl sulfoxide, containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte, with a mercury pool cathode and a platinum anode; a potential of −1.8 V was applied between the working and the counter electrode (also used as a reference) for 15 min. The reduction potential was determined by polarographic experiments using an Amel[41] Model 463 polarograph. Preliminary, slow potential sweeps indicated that this potential was well into the limiting current region.

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(41) Amel, Milano, Italy.

Acid-Catalyzed Ring Opening Reactions of Episulfoxides[1]

Kiyosi Kondo,* Akira Negishi, and Iwao Ojima

Contribution from Sagami Chemical Research Center,
3100 Onuma, Sagamihara, 229 Japan.

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Abstract: The acid-catalyzed ring opening reactions of episulfoxides in various solvents have been studied. The reaction of ethylene episulfoxide (**1**) in methanol in the presence of sulfuric acid produced thiol sulfinate **2a**, while that of **1** in ethyl mercaptan afforded disulfide **5**. The orientational effect of nucleophiles in the ring openings of unsymmetrically substituted episulfoxides, *i.e.*, **7** and **10**, were also investigated in several alcohols, ethyl mercaptan, and mixed solvents. The structural analyses of the products obtained from *cis*- and *trans*-butene episulfoxides (**14** and **15**) in methanol demonstrated that the reactions proceeded stereospecifically with inversion of configuration at the point of attack. These results are discussed in terms of a "push–pull" mechanism.

Ethylene episulfoxide (**1**) was prepared by Hartzell and Paige for the first time in 1966.[2] The ring opening reaction of **1** under acidic conditions was also noted by these authors, while they did not try to examine the structure of the product. Two years later, Manser and Tillett[3] studied the kinetics of acid-catalyzed hydrolysis of **1** and proposed an A-2 mechanism for the reaction by comparing the value of activation entropy with those of other three-membered heterocycles. These studies, however, do not seem to reveal completely the scope of the titled reaction. Our successful preparation and isolation of pure episulfoxides bearing various substituent(s)[4] enabled us to investigate the product composition and mechanistic details of the acid-catalyzed ring openings of episulfoxides.

Results

Structure of the Products. Treatment of ethylene episulfoxide (**1**) in methanol in the presence of 1 drop of concentrated sulfuric acid at 0–5° for 2 hr resulted in the formation of β-methoxyethanethiol β-methoxyethanesulfinate (**2a**) in 97% yield. The structural assignment of **2a** was based on its following spectra and elemental analyses.

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