

## Kinetics of the Reaction of 1,3-Dinitrobenzene with Methoxide Ion in Methanol Solution. Part II.<sup>1</sup> The Role of Nitroso-derivatives in the Electron-transfer Mechanism

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In the reaction of 1,3-dinitrobenzene and *m*-nitronitrosobenzene with MeO<sup>-</sup> to yield *trans*-3,3'-dinitroazoxybenzene, an intermediate species was observed, the kinetics of formation and decomposition of which were followed as a function of temperature (30–47.2 °C) and MeO<sup>-</sup> concentration (3–5M). An intermediate of the same kind was also detected in the reaction of *p*-nitronitrosobenzene with MeO<sup>-</sup>. The suggested structure for this species and the proposed reaction scheme are consistent with the experimental data and kinetic parameters. The role of nitroso-derivatives in the electron-transfer mechanism has thus been fully interpreted.

THOUGH of considerable interest, the mechanism of the reduction of the nitro-group in nitroaromatic compounds by alkoxide ions is little understood. Previously<sup>1</sup> the kinetics of the redox reaction of 1,3-dinitrobenzene (*m*-DNB) with methoxide ion to yield *trans*-3,3'-dinitroazoxybenzene were examined. In the concentration range 0.14–2.3M-MeO<sup>-</sup> the rate constants  $k_1$  for the transformation of *m*-DNB into the product were a linear function not of the concentration of methoxide ion ( $c_{\text{MeO}^-}$ ) but instead of its kinetic activity ( $a_{\text{MeO}^-}$ ; for the calculation of the kinetic activity of methoxide ion, see refs. 1 and 2) ( $k_1 = ka_{\text{MeO}^-}$ ). No spectrophotometric or other experimental evidence for intermediates was found in this range of alkoxide concentration. When the concentration of methoxide ion was increased to 3–5M, the formation of two intermediate species was detected.

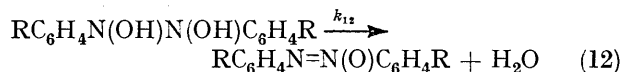
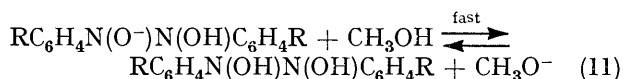
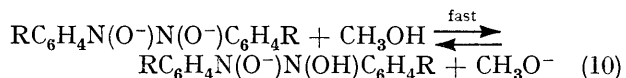
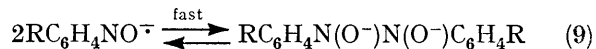
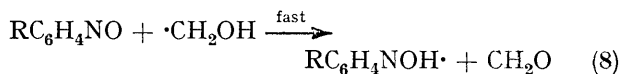
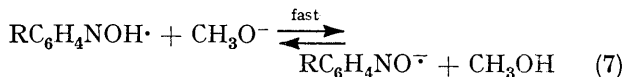
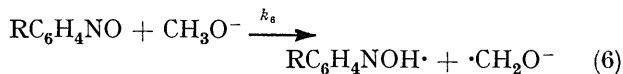
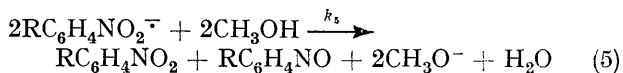
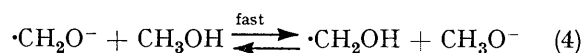
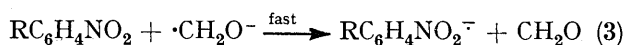
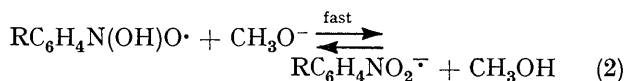
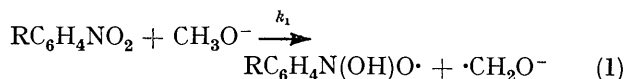
An intermediate species (I) exhibited an absorption band at *ca.* 275 nm; its concentration passed through a maximum and then decreased more slowly, evolving towards the product. The pseudo-first-order rate constant ( $k_3$ ) for the transformation (I) → *trans*-3,3'-dinitroazoxybenzene varied linearly at 40 °C with methoxide ion concentration up to the highest value investigated, while the rate constant ( $k_2$ ) for the formation of (I) was equal to that for disappearance of *m*-DNB ( $k_1$ ).

An intermediate species (II) was also observed with an absorption band at 495 nm, and was shown to be the radical anion of *m*-DNB. On the basis of the rate constants for the formation ( $k_4$ ) and decomposition ( $k_5$ ) of species (II) ( $k_4 = k_2 > k_5$  at  $c_{\text{MeO}^-} \approx 3\text{M}$ ) it was concluded that the radical anion of *m*-DNB was the first intermediate formed in the reaction between *m*-DNB and MeO<sup>-</sup>. The mechanism (1)–(12) has been proposed.

Species (I; R = *m*-NO<sub>2</sub>) was also observed during the reaction of 3-nitronitrosobenzene (*m*-NNB) with concentrated solutions of methoxide ion (>3M). In this paper, the influence of temperature and methoxide ion concentration on the rate constants  $k_3$  was systematically examined during the reaction between *m*-DNB and methoxide ion over the concentration range for which detection of species (I; R = *m*-NO<sub>2</sub>) is possible.

The decomposition of species (I; R = *m*-NO<sub>2</sub>) was also followed starting from *m*-NNB as substrate, in order to ascertain the role of the nitroso-derivative in

the reaction mechanism. Further, the kinetics of the reaction of 4-nitronitrosobenzene (*p*-NNB) with methoxide ion, during which an intermediate species (I;



R = *p*-NO<sub>2</sub>) is formed in a way analogous to that of the *meta*-derivative, were investigated, with the purpose of obtaining more information.

### EXPERIMENTAL

**Materials.**—3- and 4-Nitronitrosobenzene, 1,3-dinitrobenzene, and other reagents and solvents were prepared and/or purified as described previously.<sup>1–3</sup>

**Kinetic Procedure.**—Solutions were prepared as previously<sup>1</sup> or by mixing a small volume of a concentrated stock solution of substrate with 0.3–5.5M-MeONa in

<sup>1</sup> Part I, I. R. Bellobono, A. Gamba, G. Sala, and M. Tamperri, *J. Amer. Chem. Soc.*, 1972, **94**, 5781.

<sup>2</sup> I. R. Bellobono and G. Sala, *J.C.S. Perkin II*, 1972, 169.

<sup>3</sup> A. Gamba and I. R. Bellobono, *Gazzetta*, 1972, **102**, 445.

TABLE 1

Kinetic coefficients for the formation ( $k_2$ ) and decomposition ( $k_3$ ) of species (I; R = *m*-NO<sub>2</sub>) for the reaction between 1,3-dinitrobenzene and methoxide ion in methanol solution

	Temperature 30 °C								
$c_{\text{MeO}^-}/M$	2.42	2.72	3.01	3.12	3.22	3.50	4.00	4.44	4.96
$10^5 k_1/s^{-1}$	$0.45 \pm 0.05$	$0.98 \pm 0.09$				$7.95 \pm 0.03$			
$10^5 k_2/s^{-1}$	$0.48 \pm 0.04$	$0.95 \pm 0.08$	$2.12 \pm 0.06$	$3.15 \pm 0.07$	$4.35 \pm 0.08$	$8.33 \pm 0.19$	$31.4 \pm 1.5$	$115 \pm 9$	
$10^5 k_3/s^{-1}$			$1.41 \pm 0.05$	$1.56 \pm 0.06$	$1.68 \pm 0.08$	$1.95 \pm 0.07$	$1.85 \pm 0.09$	$1.62 \pm 0.07$	$1.28 \pm 0.08$
$10^5 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$		$1.00 \pm 0.05$							
	Temperature 40 °C								
$10^5 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$		$2.50 \pm 0.11$							
	Temperature 47.2 °C								
$c_{\text{MeO}^-}/M$	2.39	2.60	2.81	3.22	3.48	3.60	4.43	5.01	
$10^5 k_2/s^{-1}$	$2.15 \pm 0.07$	$3.54 \pm 0.06$	$5.37 \pm 0.08$	$16.3 \pm 0.8$	$22.9 \pm 0.9$	$46.9 \pm 1.3$	$286 \pm 18$	$958 \pm 31$	
$10^5 k_3/s^{-1}$				$7.69 \pm 0.28$	$8.56 \pm 0.34$	$9.21 \pm 0.48$	$13.3 \pm 0.7$	$15.6 \pm 0.8$	
$10^5 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$		$4.68 \pm 0.26$							

MeOH. The concentration of substrate after appropriate dilution was  $5.0\text{--}8.0 \times 10^{-5}M$ . Kinetic runs were followed

TABLE 2

Kinetic coefficients for the decomposition ( $k_3$ ) of species (I; R = *m*-NO<sub>2</sub>) during the reaction between 3-nitro-nitrosobenzene and methoxide ion in methanol solution

	Temperature 47.2 °C				
$c_{\text{MeO}^-}/M$	3.36	4.10	4.36	4.43	4.60
$10^5 k_3/s^{-1}$	$7.25 \pm 0.46$	$10.0 \pm 0.6$	$11.7 \pm 0.7$	$11.9 \pm 0.7$	$13.2 \pm 0.7$
$10^5 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$			$4.93 \pm 0.29$		

directly in thermostatted spectrophotometric cells. Pseudo-first order rate constants for the disappearance of *m*-DNB ( $k_1$ ) and for the formation ( $k_2$ ) and decomposition ( $k_3$ ) of

were measured at 30.0 and 47.2 °C for the reaction between *m*-DNB and 3—5M-MeO<sup>-</sup> in methanol solution. Results are reported in Table 1.

The same species (I; R = *m*-NO<sub>2</sub>), with an absorption maximum at *ca.* 275 nm in methanol solutions containing MeONa, was also observed during the reaction between *m*-NNB and 3—5M-MeO<sup>-</sup>. Rate constants ( $k_3$ ) for the decomposition of this species, starting from *m*-NNB as substrate, were also measured. Results are reported in Table 2.

Rate constants for the formation ( $k_6$ ) and decomposition ( $k_3$ ) of species (I; R = *p*-NO<sub>2</sub>), which has an absorption maximum at *ca.* 380 nm in methanolic sodium methoxide solution were obtained similarly for the reaction between *p*-NNB and 0.3—1.6M-MeO<sup>-</sup>.

TABLE 3

Kinetic coefficients for the formation ( $k_6$ ) and decomposition ( $k_3$ ) of species (I; R = *p*-NO<sub>2</sub>) for the reaction between 1,4-nitronitrosobenzene and methoxide ion in methanol solution

$c_{\text{MeO}^-}/M$	0.330	0.430	0.780	0.970	1.18
	Temperature 0.8 °C				
$10^3 k_6'/l \text{ mol}^{-1} \text{ s}^{-1}$			$5.13 \pm 0.35$		
$10^4 k_3/l \text{ s}^{-1}$	$4.25 \pm 0.18$	$4.60 \pm 0.26$	$6.30 \pm 0.38$	$6.80 \pm 0.35$	$7.65 \pm 0.29$
$10^4 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$			$4.00 \pm 0.20$		
	Temperature 12.5 °C				
$10^2 k_6'/l \text{ mol}^{-1} \text{ s}^{-1}$			$1.26 \pm 0.12$		
	Temperature 31.7 °C				
$10^2 k_6'/l \text{ mol}^{-1} \text{ s}^{-1}$			$4.52 \pm 0.29$		
$10^3 k_3/s^{-1}$	$3.42 \pm 0.16$	$3.62 \pm 0.21$	$4.93 \pm 0.32$	$5.30 \pm 0.36$	$5.83 \pm 0.27$
$10^3 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$			$2.92 \pm 0.19$		
	Temperature 48.8 °C				
$10^3 k_3/s^{-1}$	$8.62 \pm 0.39$	$9.50 \pm 0.49$	$12.7 \pm 1.1$	$14.5 \pm 1.2$	$16.3 \pm 0.9$
$10^3 k_3'/l \text{ mol}^{-1} \text{ s}^{-1}$			$8.90 \pm 0.62$		

species (I; R = *m*-NO<sub>2</sub>) during the reaction between *m*-DNB and MeO<sup>-</sup> were obtained as indicated previously.<sup>1</sup> The same procedure was adopted to obtain pseudo-first-order constants  $k_3$  for the decomposition of species (I; R = *m*-NO<sub>2</sub>) starting from *m*-NNB as substrate, and for the formation ( $k_6$ ) or decomposition ( $k_3$ ) of species (I; R = *p*-NO<sub>2</sub>) starting from *p*-NNB as substrate.

#### RESULTS AND DISCUSSION

Pseudo-first-order rate constants for the formation ( $k_2$ ) and decomposition ( $k_3$ ) of species (I; R = *m*-NO<sub>2</sub>)

Results are summarized in Table 3, where  $k_6'$  denotes the second-order rate constant obtained in terms of the kinetic activity of methoxide ion from the slope of the experimental plot of  $k_6$  vs.  $a_{\text{MeO}^-}$ .

The constants  $k_3$  show a linear dependence on methoxide concentration covering the whole set of experimental values at 40 °C and 47.2 °C during the reactions of *m*-DNB and *m*-NNB, while for this same reaction the linear range at 30 °C is rather restricted (3—3.5M-MeO<sup>-</sup>). During the reaction of *p*-NNB with methoxide ion, on

the other hand, the linear correlation of  $k_3$  and methoxide concentration is much more extended ( $c_{\text{MeO}^-} > 0.1\text{M}$ ). The reason is that pseudo-first-order constants for the production of the intermediate species (I) ( $k_2$  when starting from nitro-compound,  $k_6$  when starting from nitroso-derivative) are equal to those for disappearance of the substrate (compare  $k_1$  and  $k_2$  in Table 1) and are not a linear function of methoxide concentration but of its kinetic activity, while pseudo-first-order constants  $k_3$  for the decomposition of species (I) generally show a simple linear dependence on methoxide ion concentration. These latter constants could only be measured under conditions where the decomposition of (I) was slower than its formation.

In the reaction between *m*-DNB and  $\text{MeO}^-$   $k_2/k_3$  reaches unity at a concentration of *ca.*  $2.88\text{M-MeO}^-$  at  $47.2^\circ\text{C}$ ,  $2.89\text{M-MeO}^-$  at  $40^\circ\text{C}$ ,<sup>1</sup> and  $2.80\text{M-MeO}^-$  at  $30^\circ\text{C}$ . Therefore the value of sodium methoxide concentration, at which all rate constants  $k_1$  (disappearance of *m*-DNB and formation of product),  $k_2$  [formation of species (I; R = *m*-NO<sub>2</sub>)], and  $k_3$  [decomposition of species (I; R = *m*-NO<sub>2</sub>) into product] are equal, is independent of temperature within the limits of experimental uncertainty. Above this concentration, decomposition of species (I; R = *m*-NO<sub>2</sub>) is the rate-determining process, while below it the formation of the radical anion of *m*-DNB is the slow step.

In the reaction between *p*-NNB and  $\text{MeO}^-$   $k_6/k_3$  is  $>1$  at concentrations exceeding *ca.*  $0.1\text{M-MeO}^-$ , so that the linear dependence of  $k_3$  on  $c_{\text{MeO}^-}$  can be easily checked and explored (*cf.* Table 3). In the linear portion of the graph of  $k_3$  vs.  $c_{\text{MeO}^-}$  the second-order rate constants  $k_3'$  can be calculated. Their values, when starting from *m*-DNB, *m*-NNB, or *p*-NNB as substrates, are reported in Tables 1, 2, and 3 respectively.

The constants  $k_3$  and  $k_3'$  for the reaction of *m*-DNB with  $\text{MeO}^-$  (Table 1) agree fairly well with the corresponding values shown by the reaction between *m*-NNB and  $\text{MeO}^-$  (Table 2). This is consistent with the fact that 3-nitronitrosobenzene is the precursor of species (I; R = *m*-NO<sub>2</sub>) in both reactions. The role played by the nitroso-derivative in the reaction scheme (1)–(12) is thus confirmed.

A structure which may be suggested for species (I) is *NN'*-dihydroxy-*NN'*-diphenylhydrazine (with the appropriate R substituents); but it is not easy to establish unequivocally whether it is in the acid form ( $\text{H}_2\text{A}$ ), or the mono- ( $\text{HA}^-$ ) or di-conjugate base ( $\text{A}^{2-}$ ). If the linear dependence of  $k_3$  on methoxide ion concentration may be interpreted as base catalysis in terms of sodium methoxide concentration, then proton transfer from an oxygen atom of species (I) and elimination of water [equation (12)] should represent the slow process, and species (I) may be identified with  $\text{H}_2\text{A}$ .

From the temperature variation of  $k_3'$  kinetic parameters for the decomposition of species (I; R = *m*-NO<sub>2</sub>) during the reaction between *m*-DNB and  $\text{MeO}^-$  were obtained:  $\Delta E^* = 17.1 \pm 0.4$  kcal mol<sup>-1</sup>,  $\log A = 7.35 \pm 0.1$  ( $A$  in l mol<sup>-1</sup> s<sup>-1</sup>),  $\Delta S^* = -27.9 \pm 0.5$  cal mol<sup>-1</sup> K<sup>-1</sup> (at 311.8 K). For the decomposition of species (I; R = *p*-NO<sub>2</sub>)  $\Delta E^* = 11.3 \pm 1.8$  kcal mol<sup>-1</sup>,  $\log A = 5.57 \pm 0.3$  ( $A$  in l mol<sup>-1</sup> s<sup>-1</sup>),  $\Delta S^* = -35.1 \pm 1.5$  cal mol<sup>-1</sup> K<sup>-1</sup> (at 314 K). The low entropy of activation for the decomposition of species (I) is compatible with the suggested structure of this intermediate.

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