

KINETICS AND MECHANISM OF REACTION OF 2,4-DINITROBENZALDEHYDE WITH HYDROXIDE ION

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The reaction of 2,4-dinitrobenzaldehyde with hydroxide ion in water is first order in the substrate. The reaction order in hydroxide ion varies from one to two at lower and higher OH^- concentrations, respectively. The reaction mechanism has been suggested, the $\text{p}K_a$ value of reaction product 2-nitro-4-nitrosophenol and the equilibrium constant of formation of the Meisenheimer adduct from 2-nitro-4-nitrosophenoxide and hydroxide ion have been determined.

The reaction of 2-(2,4,6-trinitrophenylamino)carboxylic esters with methoxide ion in methanol produces 4,6-dinitro-2-nitrosoaniline¹. Similarly methyl *N*-methyl-*N*-(2,4,6-trinitrophenyl)glycinate and methyl *N*-methyl-*N*-(2,4-dinitrophenyl)glycinate react with methoxide to give *N*-methyl-4,6-dinitro-2-nitrosoaniline² and *N*-methyl-4-nitro-2-nitrosoaniline³, respectively. All the reactions mentioned were studied from the point of view of kinetics¹⁻³, and the following mechanism was suggested: An intramolecular attack of the carbonyl carbon atom by the nitrogen atom of secondary or tertiary amino group produces an unstable aziridinone derivative which is opened by an intramolecular attack of the oxygen atom of *o*-nitro group. The subsequent E_2 elimination, which in fact is an oxidation-reduction reaction, produces a substituted anilide of glyoxylic acid which is solvolyzed by methanol to give the products: substituted 4-nitro-2-nitrosoaniline and a derivative of glyoxylic acid.

An apparently similar reaction of 2,4-dinitrobenzaldehyde with hydroxide ion in water produces formiate anion and 2-nitro-4-nitrosophenol⁴. The reaction kinetics were not studied. The authors⁴ suggested a reaction mechanism according to which the reaction should be of the second order in the substrate.

The aim of the present paper is to study the kinetics of the reaction of 2,4-dinitrobenzaldehyde with hydroxyl ion and contribute to elucidation of the reaction.

EXPERIMENTAL

2,4-Dinitrobenzaldehyde (Aldrich), m.p. 68 – 70 °C, ref.⁵ gives m.p. 71 – 72 °C. 2-Nitro-4-nitrosophenol was prepared by a known way⁴ from 2,4-dinitrobenzaldehyde. Yield 50%, m.p. 65 – 68 °C,

ref.⁴ gives 65 – 66 °C. ¹H NMR spectrum (Bruker AM 400, 400.13 MHz, CDCl₃): 11.17 s, 1 H (OH); 9.14 d, 1 H (H-3, *J* = 2.0 Hz); 7.74 dd, 1 H (H-5, *J* = 8.9 Hz); 7.30 d, 1 H (H-6). ¹³C NMR (Bruker AM 400, 100.62 MHz, CDCl₃): 159.81, 159.73 (C-1 and/or C-4), 133.06 (C-2), 124.83, 124.05 (C-3 and/or C-5), 120.72 (C-6).

The measurements of kinetics and those of dissociation constants were carried out with a diode array spectrophotometer Hewlett–Packard 8452A and a spectrophotometer Unicam SP-800 at 25 °C. The stock solution of 2,4-dinitrobenzaldehyde (0.01 mol l⁻¹) was prepared in dry tetrahydrofuran free of peroxides. The solution was kept in dark at 0 °C.

Using a microdoser, 10 μl 2,4-dinitrobenzaldehyde stock solution was added to 2 ml thermostated NaOH solution of known concentration (the NaOH solutions were prepared in redistilled water free of oxygen) and mixed. The absorbance of the solution was measured at the wavelength of 400 nm (λ_{\max} of anion of product) for a period of ca 4 half-lives. During the measurement the cell was tightly closed. The rate constants *k*_{obs} were obtained with the help of a PC-AT and a published program⁶.

The p*K*_a value of 2-nitro-4-nitrosophenol was determined spectrophotometrically using formiate buffers (pH 2.9 – 4.3). The ionic strength *I* = 1.0 mol l⁻¹ was adjusted by adding a KCl solution; the concentration of 2-nitro-4-nitrosophenol was 5 · 10⁻⁴ mol l⁻¹. The measurements were carried at the wavelength of 400 nm. The pH values of solutions were measured with a digital pH meter OP-211/1 calibrated with a tartrate and a phosphate buffers (pH 3.56 and 7.00, respectively) using a combined glass and silver chloride electrode.

The equilibrium constant of the reaction of 2-nitro-4-nitrosophenoxide with hydroxide ion was determined in aqueous solution of sodium hydroxide (0.045 – 1.8 mol l⁻¹) without adjusting the ionic strength, the initial concentration of 2-nitro-4-nitrosophenoxide being 5 · 10⁻⁴ mol l⁻¹. The measurement was carried out at 400 nm. The equilibrium constant was obtained from Eq. (1).

$$\text{p}K = \log [I_b]/[I_c] + \log [\text{OH}^-] \quad (1)$$

The concentration ratio of 2-nitro-4-nitrosophenoxide anion ([I_b]) to its adduct with hydroxide ion ([I_c]) was determined from the absorbances (Eq. (2), where *A*_i and *A*_o are the absorbances of the anion and adduct, respectively).

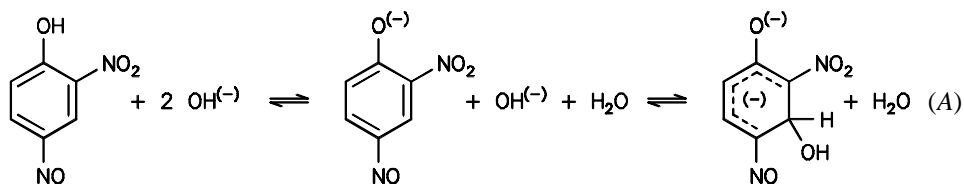
$$[I_c]/[I_b] = (A_i - A)/(A - A_o) \quad (2)$$

RESULTS AND DISCUSSION

Forbes and Gregory⁴ identified 2-nitro-4-nitrosophenol as the product of reaction of 2,4-dinitrobenzaldehyde with aqueous hydroxide. The identity was confirmed by preparing derivatives of the product. We have proved that 2-nitro-4-nitrosophenol is the main product of the said reaction at the conditions of kinetic experiments. By comparing the electronic spectrum of the authentic substance with those of the product formed during kinetic experiments it was proved that the yields of 2-nitro-4-nitrosophenol were 98 ± 2% and 96 ± 3% at the NaOH concentrations of 0.2 and 1.0 mol l⁻¹, respectively. At still higher NaOH concentrations the comparison is not precise since the primary adduct undergoes a consecutive reaction, which lowers the *A*_∞ value in the kinetic runs.

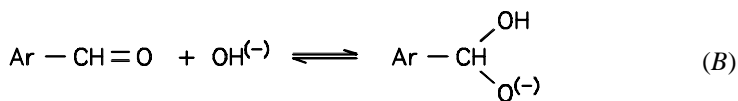
2-Nitro-4-nitrosophenol is a strong acid. Its pK_a is 3.37 in water, i.e. it is five times as acidic as 2,4-dinitrophenol (ref.⁷ gives pK_a 4.08 at the ionic strength of 0.1 mol l⁻¹).

In solutions of hydroxide, 2-nitro-4-nitrosophenoxide adds hydroxide ion to give a Meisenheimer adduct. From analogy with the reaction of 2,4-dinitrophenoxide⁸ it can be presumed that this is the so-called 1,3-adduct (Eq. (A)). The equilibrium constant of addition of hydroxide ion is $pK = 0.9$.



In the reaction of 2,4-dinitrobenzaldehyde with hydroxide ion, the time dependences of $\log(A_\infty - A_t)$ are linear with high values of regression coefficients in the whole range of substrate concentration studied ($10^{-5} - 2 \cdot 10^{-4}$ mol l⁻¹). Hence the reaction is of the first order in the substrate. Moreover it was found that the reaction order in hydroxide ion changes: it is about 1 at the lowest NaOH concentrations and increases with increasing concentration, the reaction rate being linearly dependent on the square of hydroxyl ion concentration at the NaOH concentrations above 1 mol l⁻¹ (Table I, Fig. 1). The reaction rate is defined by Eq. (3), where $[S^-]$ is the concentration of 2,4-dinitrobenzaldehyde hydrate anion (Eq. (B)) which is approximately equal to the analytical concentration of the aldehyde. The rate constants have the following values: $k_1 = (2.0 \pm 0.5) \cdot 10^{-3}$ l mol⁻¹ s⁻¹ and $k_2 = (1.2 \pm 0.1) \cdot 10^{-2}$ l² mol⁻² s⁻¹.

$$v = k_{\text{obs}}[S^-] = (k_1[\text{OH}^-] + k_2[\text{OH}^-]^2)[S^-] \quad (3)$$



The reaction mechanism suggested by Forbes and Gregory⁴ is presented in Scheme 1. The rate-limiting step consists either in a nucleophilic attack of carbonyl carbon atom in one substrate molecule by oxygen atom of nitro group of 1,1-adduct of another substrate molecule with hydroxide ion or in splitting off of formic acid from the intermediate formed. Hence the reaction should be of the second order in the substrate. In the

medium of the reaction, the starting 2,4-dinitrobenzaldehyde, like other aromatic aldehydes with strongly electron-withdrawing substituents⁹⁻¹¹, is almost completely transformed into its hydrate anion (Eq. (B)). With respect to the fact that 2,4-dinitrobenzaldehyde enters the reaction as an anion, the transition state of the bimolecular mechanism by Forbes and Gregory⁴ should have three or even four negative charges. Each of the not given transition states on the pathway from 2,4-dinitrobenzaldehyde hydrate anion to 2-nitro-4-nitrosophenol carries one negative charge. That means that the formation of 2-nitro-4-nitrosophenol according to the mechanism by Forber and

TABLE I

Rate constants of reaction of 2,4-dinitrobenzaldehyde with sodium hydroxide in water at 25 °C

[OH ⁻], mol l ⁻¹	$k_{\text{obs}} \cdot 10^3, \text{s}^{-1,a}$	[OH ⁻], mol l ⁻¹	$k_{\text{obs}} \cdot 10^3, \text{s}^{-1,a}$
0.2	1.4	1.2	19.8
0.3	2.0	1.3	22.8
0.4	3.0	1.4	25.6
0.5	4.1	1.5	29.3
0.6	5.9	1.6	33.0
0.7	7.3	1.7	38.8
0.8	9.1	1.8	42.0
0.9	10.7	1.9	46.5
1.0	13.0	2.0	52.0
1.1	16.2		

^a $k \pm 10\%$; [2,4-dinitrobenzaldehyde] = $5 \cdot 10^{-5}$ mol l⁻¹.

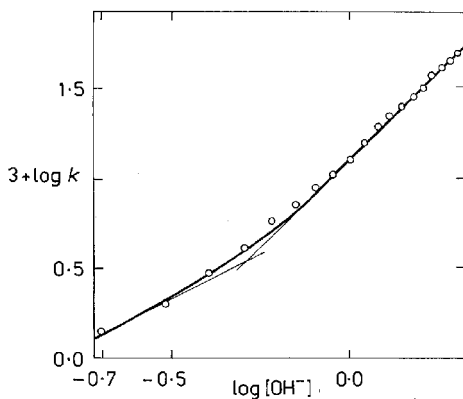
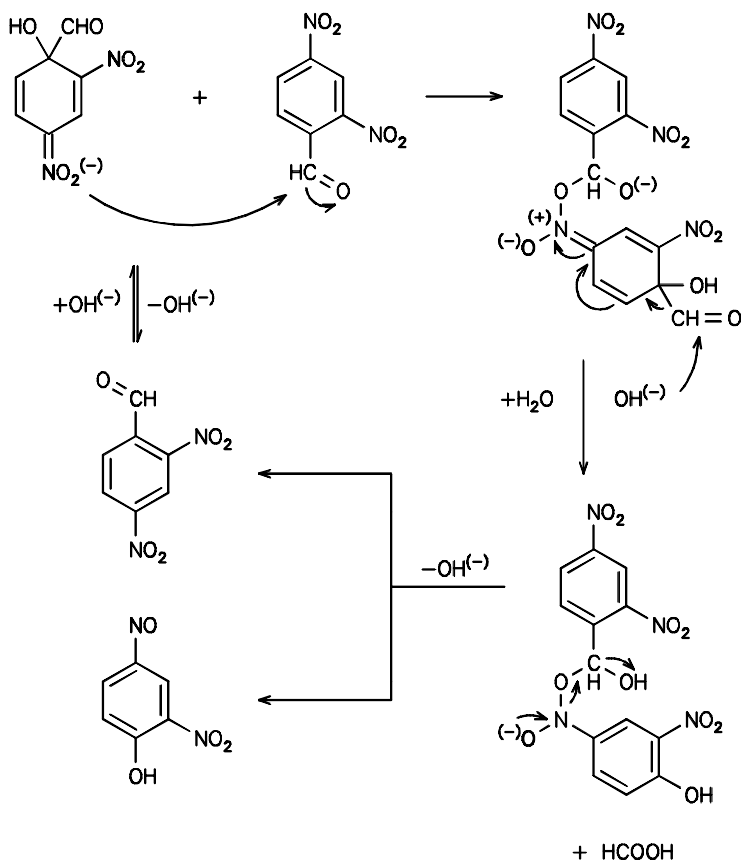


FIG. 1

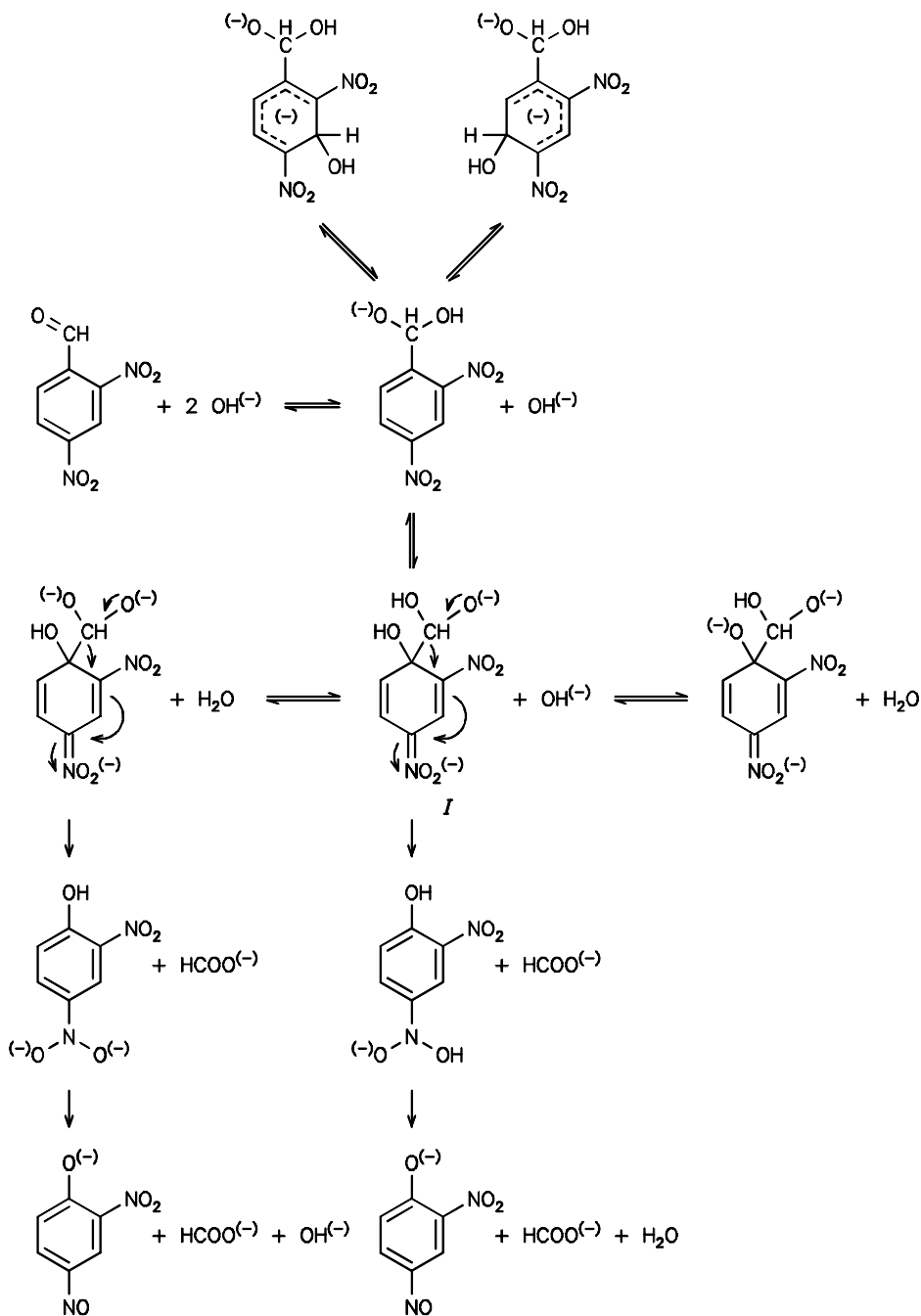
Dependence of $\log k_{\text{obs}}$ vs $\log [\text{OH}^-]$ for reaction of 2,4-dinitrobenzaldehyde with NaOH in water at 25 °C

Gregory should be acid catalyzed. If a proton were split off from those transition states (they would carry two charges each), the reaction would proceed as a noncatalyzed one. Forbes and Gregory⁴ suggested their mechanism on the basis of identification of the reaction product only. The intermolecular course considered contradicts the intramolecular reaction of *N*-phenylglycine derivatives which was proved by kinetic studies¹⁻³.



SCHEME 1

On the basis of kinetic measurements we have suggested the reaction mechanism expressed in Scheme 2. In NaOH solution, 2,4-dinitrobenzaldehyde is immediately transformed into its hydrate anion. This species reversibly adds a hydroxide ion at the position 3, 5 or 1 to give the respective Meisenheimer adducts. Only the addition at the 1 position leads to a consecutive reaction. By action of another hydroxide ion, the



SCHEME 2

anionadduct formed splits off an acidic proton either from the hydroxyl group at the ring or in the side chain. Only the second reaction mentioned leads to the product. The rate-limiting step consists either in this splitting off of the proton or in subsequent splitting off of formiate anion. Finally, the hydroxyl group is split off in a reaction with water to give the anion of 2-nitro-4-nitrosophenol. At low concentrations of hydroxide ion, another reaction pathway also becomes significant, viz. splitting off of formic acid from the dianion of adduct *I*. In the given reaction medium, the 2-nitro-4-nitrosophenol formed is immediately transformed into the phenoxide and its adduct with hydroxide ion.

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