

Kinetics and Mechanism leading to Dimeric Redox Products of 4-Nitrosobenzaldehyde in Alkaline Dioxane-Water Media

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Dedicated to Prof. Dr. Y. Iskander on the occasion of his 70th birthday

A Cannizzaro disproportionation reaction of 4-nitrosobenzaldehyde (I) and sodium hydroxide in dioxane-water media is kinetically studied by UV-Vis. absorption spectroscopy. The reaction did not give the expected products, namely 4-nitrosobenzyl alcohol and 4-nitrosobenzoic acid, but gave equimolecular quantities of 4,4'-diformylazoxybenzene (II) and 4,4'-dicarboxyazoxybenzene (III) and was found to exhibit third-order kinetics, second-order in aldehyde and first-order in base. The rate constants as well as the activation thermodynamic parameters were calculated for different temperatures and different dioxane-water compositions, and discussed on the bases of dielectric constant, viscosity and heat of mixing of the medium components. The rate determining step is a hydride ion transfer from the adduct (formed from the attack of one hydroxide ion on molecule of I) to another molecule of I. A mechanism is given to explain the formation of the end reaction products.

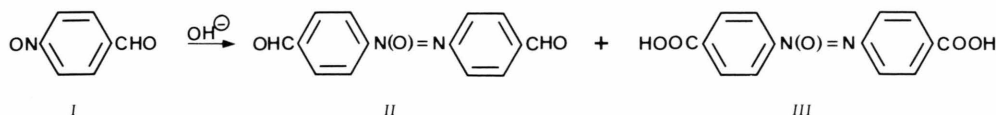
Introduction

The change of nitroaromatics into azoxy- and azobenzene structures has been known for many decades [1–5]. 4-Nitrophenylacetic acid reacts in aqueous methanolic alkali to give a mixture of dioxalo-azo and -azoxybenzenes [6] while the action of aqueous alkali on 4-nitrobenzyl-pyridinium salts [7] or -thioacids [8] gives 4,4'-diformylazoxybenzene (II). The reported mechanisms were only schematic speculations that lead to the end products. 4-Nitrosobenzaldehyde (I) was expected to be a precursor for II [8]. Therefore, in the present work the reaction of sodium hydroxide with I in dioxane-water media was studied in order to see whether the expected products out of the Cannizzaro reaction, namely 4-nitrosobenzyl alcohol and 4-nitrosobenzoic acid, could change in the reaction medium to give the final reaction products. In fact sodium hydroxide reacts with α -(4-nitrobenzylthio)acetic acid to give 4,4'-diformylazoxybenzene (II), 4,4'-dicarboxyazoxybenzene and a nitron acid [9].

Experimental

Materials

4-Nitrosobenzaldehyde was prepared by a modification of the method described by Alway [10]: 4.0 g (0.026 M) of 4-nitrobenzaldehyde in 50 ml methanol and 6.0 ml glacial acetic acid was treated with 4.0 g zinc dust, in portions, with stirring at 60 °C. The produced yellow-orange solution was oxidised by heating with 50 ml of 10% potassium dichromate solution and 50 ml of 10% sulfuric acid for 20 min. The solution was diluted with water, and the precipitated solid was steam distilled, which gave 4-nitrosobenzaldehyde (3.1 g) which after three crystallisations from acetone gave a product with melting point 139–140 °C ([10] m.p. 137.5), IR (KBr disk): 1700 (C=O), 1600 cm⁻¹ (N=O); UV (CH₃OH): λ_{\max} = 290 nm log ϵ = 3.996; ¹H-NMR (CDCl₃): δ = 8.2–8.4 (m, 4H, aromatic), 10.98 (s, H, CHO).



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Treatment of 4-Nitrosobenzaldehyde with Sodium Hydroxide

25 ml of 0.01 M of 4-nitrosobenzaldehyde were added to 25 ml 0.4 N sodium hydroxide solution. The mixture was heated to 60 °C for 5 min. Cold water was added and the precipitated solid was dried and crystallised from dry benzene in yellow needles m.p. 193 °C alone or mixed with an authentic specimen of 4,4'-diformylazoxybenzene ([11] m.p. 193–194 °C). (Found: C, 65.9; H, 3.9; N, 11.07. Calc. for C₁₄H₁₀N₂O₃: C, 66.1; H, 3.9; N, 11.02%). IR (KBr disk): 1700 (C=O), 1425 (N=N) and 1295 cm⁻¹ (N–O); UV (dioxane) λ_{max} = 332 nm log ϵ = 4.44; ¹H-NMR (d⁶-DMSO): δ = 8.12–8.4 (m, 8H, aromatic), 10.1–10.2 (d, 2H, CHO). Acidification of the alkaline filtrate with dilute sulfuric acid gave a yellow acid which was crystallised from acetic acid, m.p. > 360 °C. It was identified as 4,4'-dicarboxyazoxybenzene [6, 12].

Symmetrical 1,4-dioxane was purified as described in the literature [13, 14]. The water used in the preparation of solutions and in the kinetic runs was freshly distilled from alkaline potassium permanganate.

Kinetic Procedure

The reaction was followed by measuring the ultraviolet-visible absorption at 380 nm using a Unicam 1805 SP spectrophotometer coupled with an ultrathermostate. One ml of each of the reactant solutions, 4-nitrosobenzaldehyde (2×10^{-3} mol l⁻¹ in appropriate dioxane-water mixture) and sodium hydroxide (4×10^{-3} mole l⁻¹ in water) were separately introduced into the two parts of the two compartment cell (Hellma, 238-QS) and thermostated for 15 min. After shaking the cell contents, 5–10 sec, the absorption of the mixture was recorded at suitable time intervals.

The amount, x , of reacted 4-nitrosobenzaldehyde was calculated by applying the equation

$$x = \frac{A - l a \epsilon_1}{l [0.5 (\epsilon_2 + \epsilon_3) - \epsilon_1]},$$

where A is the absorption of the mixture, l is the cell thickness (0.437 cm), a is the initial concentration of 4-nitrosobenzaldehyde, which was always taken as 1×10^{-3} mole l⁻¹, $\epsilon_1 = 549$, $\epsilon_2 = 5143$ and $\epsilon_3 = 5200$ l mole⁻¹ cm⁻¹ are the molar extinction coefficients

of 4-nitrosobenzaldehyde (I), 4,4'-diformylazoxybenzene (II) and 4,4'-dicarboxyazoxybenzene (III) respectively.

Results and Calculations

The third order rate constant k_3 (l² mole⁻² sec⁻¹) was calculated from the equation [15, 16]

$$k_3 = \frac{1}{a t (a - b)} \cdot \frac{x}{a - x} + \frac{1}{t (a - b)^2} \ln \frac{b(a - x)}{a(a - x)},$$

where x is the concentration of the reacted 4-nitrosobenzaldehyde at time t , and a and b are the initial concentrations of 4-nitrosobenzaldehyde and sodium hydroxide, respectively. The reaction was followed to not less than 85% completion in various dioxane-water mixtures, 20–50% (w/w), at 35, 45, 55 and 65 °C.

Data for a typical run are given in Table 1, and the values of k_3 are collected in Table 2 for the indicated temperatures. A statistical least squares

Table 1. Kinetics of reaction of 1×10^{-3} M I with 2×10^{-3} M sodium hydroxide in 50.68% (w/w) dioxane-water at 35 °C.

Time [sec]	Absorbance at $\lambda = 380$ nm	k_3 [l ² mol ⁻² sec ⁻¹]
530	0.74	108.92
740	0.82	99.06
955	0.96	109.35
1185	1.08	114.78
1420	1.17	115.00
1660	1.24	112.73
1965	1.32	110.77
mean = 110.09 ± 5		

Table 2. Third-order rate constants and activation energies of the Cannizzaro reaction.

Dioxane [wt%]	k_3 [l ² mol ⁻² sec ⁻¹]				E [kJ mol ⁻¹]
	35 °C	45 °C	55 °C	65 °C	
50.68	110.1 ± 5	171.2 ± 6	298.4 ± 13	443.4 ± 18	41.02 ± 0.01
41.35	451.7 ± 35	533.1 ± 18	811.0 ± 15	1519.0 ± 11	28.73 ± 0.87
30.01	471.6 ± 23	708.7 ± 20	767.9 ± 11	1522.8 ± 17	24.26 ± 0.99
20.67	164.6 ± 13	256.9 ± 4	493.0 ± 17	712.9 ± 3	36.93 ± 1.11

Table 3. Activation thermodynamic parameters.

<i>t</i> [°C]	Parameters	Dioxane [wt%]			
		50.68	41.35	30.01	20.67
35	ΔG^\ddagger kJ mol ⁻¹	63.68	85.98	81.44	96.59
	ΔH^\ddagger kJ mol ⁻¹	38.45	26.18	21.70	34.37
	$-\Delta S^\ddagger$ J mol ⁻¹ deg ⁻¹	81.39	194.17	193.96	202.67
45	ΔG^\ddagger kJ mol ⁻¹	64.50	87.53	60.77	97.64
	ΔH^\ddagger kJ mol ⁻¹	38.37	26.10	21.62	34.28
	$-\Delta S^\ddagger$ J mol ⁻¹ deg ⁻¹	82.12	193.18	122.93	199.24
55	ΔG^\ddagger kJ mol ⁻¹	65.29	88.32	84.07	97.86
	ΔH^\ddagger kJ mol ⁻¹	38.29	26.02	21.53	34.20
	$-\Delta S^\ddagger$ J mol ⁻¹ deg ⁻¹	81.68	189.96	190.44	194.08
65	ΔG^\ddagger kJ mol ⁻¹	66.05	84.46	83.98	98.77
	ΔH^\ddagger kJ mol ⁻¹	38.20	25.93	21.45	34.12
	$-\Delta S^\ddagger$ J mol ⁻¹ deg ⁻¹	82.34	185.00	184.99	191.27

treatment [17] of the Arrhenius equation was used to calculate the activation energies *E* (cf. Table 2). The correlation coefficient values (*r*) of the linear plot of the Arrhenius equation are almost equal to unity.

The entropies, enthalpies and free energies of activation ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger , respectively were calculated from the expressions

$$\log k_3/T = 10.3187 + \frac{\Delta S^\ddagger}{19.147} - \frac{\Delta H^\ddagger}{19.147 T},$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger,$$

where ΔH^\ddagger , ΔS^\ddagger and k_3 are in J mole⁻¹, J mole⁻¹ deg⁻¹ and l² mole⁻² sec⁻¹, respectively. The activation thermodynamic parameters are collected in Table 3.

Discussion

The reaction between 4-nitrosobenzaldehyde and sodium hydroxide in dioxane-water media is a clear kinetic reaction. The absorption vs. time curves of the reaction runs are identical to that for artificial standard solutions of reactants and products (having the same concentration as the original kinetic run), indicating that the intermediates have no absorption to overlap with the reactants and products absorptions (Figure 1).

In order to get a full picture of the mechanism of such a dimeric redox system, the kinetics were studied in different media containing varying dioxane-water percentages. The reaction was found to obey a third-order rate law, second-order in 4-ni-

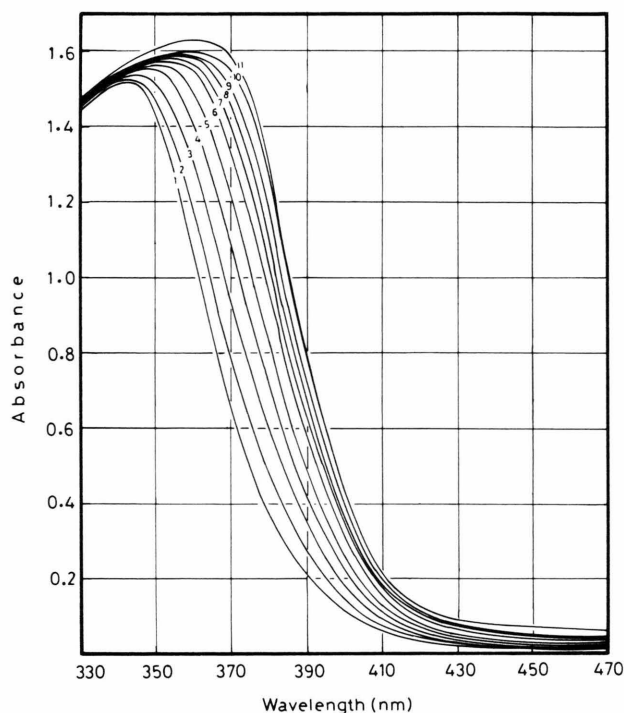
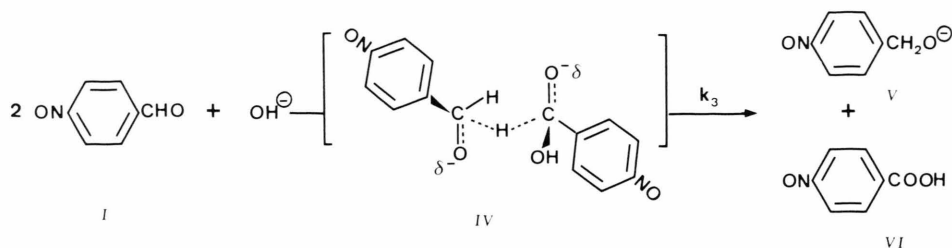


Fig. 1. The absorption spectra at different time intervals of the reaction studied in 50.68% (w/w) dioxane-water at 35 °C.

trosobenzaldehyde and first-order in sodium hydroxide.

The transition state is formed from the approach of the adduct (formed from the attack of one hydroxide ion on to the carbonyl carbon of one molecule of aldehyde (I)) to another molecule of (I). The rate determining step is the hydride ion transfer



from the adduct to the other molecule of (I) thus leading to 4-nitrosobenzylalcoholate and 4-nitrosobenzoic acid. That is, the rate determining step is the autoredox Cannizzaro reaction.

The third order rate constant values k_3 , Table 2, show a remarkable variation with solvent composition. In general, these values increase with rising the water content of the reaction medium, and a maximum was observed near 30% dioxane-water.

The increase of the rate constant with increasing dielectric constant of the reaction medium (Fig. 2) indicates that the transition state (IV) is more polar than the reactants. The carbonyl groups of both aldehyde molecules in (IV) are likely to be polarised by hydrogen bonding to water molecules [20], this increases the reaction rate with increasing the water content of the reaction medium.

The values of the dielectric constant are taken or interpolated from the data of Åkerlöf [21] for different solvent mixtures.

Application of the electrostatic theories, either ion-molecular dipole interaction [22, 23] by plotting $\log k_3$ against $1/D$, or molecular dipole-molecular dipole interaction [24, 25] by plotting $\log k_3$ against $(D-1)/(2D+1)$, gave poor linearity in the low range of the dielectric constant for all the applied temperatures. Similar behaviour had been attributed to solvent sorting or preferential solvation of the activated complex by water [26, 27]. The observation of a maximum in rate constant near 30% dioxane-water (w/w) was undoubtedly due to the participation of other factors besides the dielectric constant. The hydride ion transfer in the transition state (IV) is an intermolecular process, therefore the increase of the viscosity of the reaction medium should enhance the reaction rate. The viscosity of dioxane-water mixtures has a maximum near 30% (w/w), Table 4, which has been attributed to structure promotion [28, 29].

The mixing of dioxane and water is endothermic at high molar concentrations of dioxane but exothermic at low dioxane concentration [30, 31]. This

indicates that the mutual attraction between water and dioxane is much weaker at lower dioxane content, and that the water molecules are more readily available for solvation than in case of higher dioxane content. Thus the transition state will be more solvated at low dioxane content and hence less energetic.

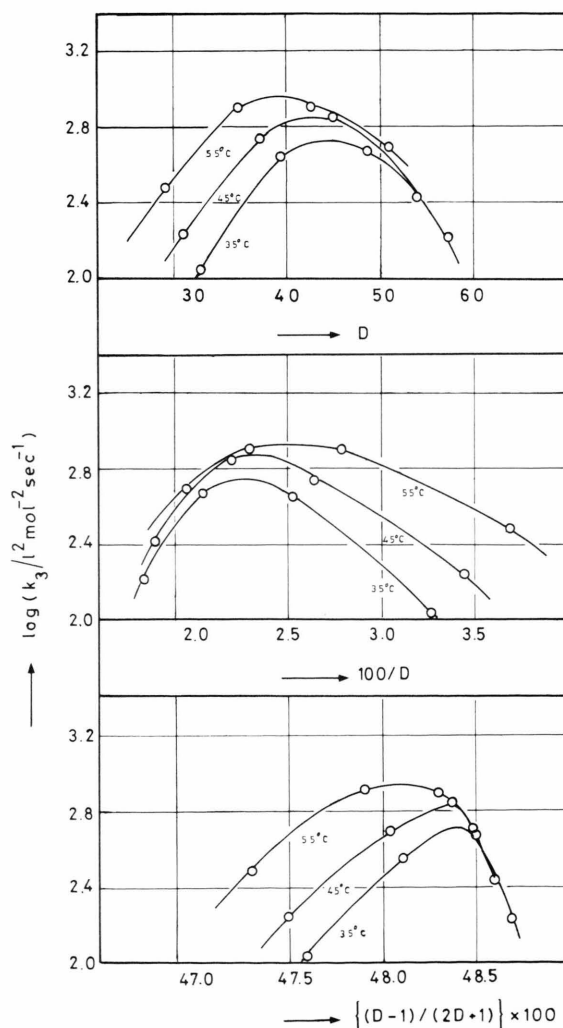


Fig. 2. Plots of the rate of the reaction against the dielectric constant of the medium.

Table 4. Heat of mixing (ΔH_m in J mol⁻¹) and viscosity (η in c.P.) of dioxane-water mixture at 25 °C.

Dioxane [mol%]	10	20	30	40	50	60	70
ΔH_m	- 523.0	- 543.9	- 351.5	- 117.1	+ 83.7	+ 292.9	435.1
η	1.59	1.90	2.00	1.83	1.60	1.42	1.38

The activation energies for different dioxane-water mixtures (cf. Table 2) lie in the range characteristic for the Cannizzaro reaction [32, 33]. The energy of activation shows a minimum at nearly 30% dioxane-water, which is also due to the solvation of the transition state (IV) and to the maximum viscosity at this solvent composition.

The thermodynamic parameters, free energies ΔG^\ddagger , enthalpies ΔH^\ddagger and entropies ΔS^\ddagger of activation are collected in Table 3. In general, ΔG^\ddagger increases as water is added and ΔH^\ddagger shows a minimum near 30% dioxane-water mixture. The entropy of activation ΔS^\ddagger has a large negative value characteristic for hydride ion transfer and decreases regularly as the transition state is organised by solvation, that is at high water concentrations.

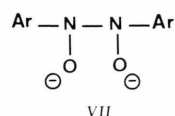
In order to give a full picture for the mechanism of such a reaction we have concentrated mainly on three steps; (i) the transformation of 4-nitrosobenzaldehyde, via Cannizzaro reaction, to 4-nitrosobenzylalcohol and 4-nitrosobenzoic acid, (ii) the transformation of 4-nitrosobenzylalcohol to 4,4'-diformylazoxybenzene and (iii) the transformation of 4-nitrosobenzoic acid to 4,4'-dicarboxyazoxybenzene.

The kinetic data, rate constants (k_3) and the activation thermodynamic parameters show that the rate determining step is the hydride ion transfer in the transition state (IV). This step leads to the formation of 4-nitrosobenzylalcohol and 4-nitrosobenzoic acid.

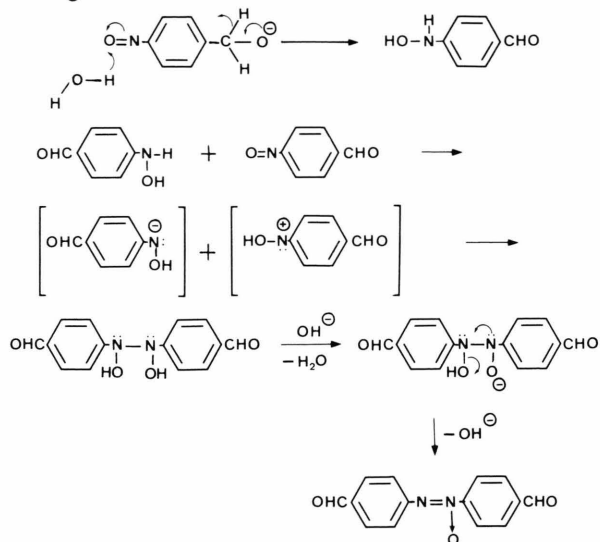
It is worth mentioning here that radical chain mechanisms have been proposed for the Cannizzaro reaction [34, 35] but were excluded because radical initiators, benzoyl or sodium peroxide, or inhibitors, hydroquinone or diphenylamine, have no effect on the rate [36]. Swain *et al.* [20] recently reported that when the reaction was carried out in deuterium oxide, the alcohol produced from the Cannizzaro reaction of benzaldehyde or formaldehyde contains no carbon-bound deuterium; this excludes all

mechanisms involving a hydride ion transfer from or to oxygen atoms.

The formation of azoxy compounds from aromatic nitroso compounds and aryl hydroxylamines, the so called azoxy coupling reaction, proceeds by way of a symmetrical intermediate with chemically equivalent nitrogen atoms [37–40], which has a structure of bis-anion (VII) in alkaline medium.



The formed 4-nitrosobenzylalcohol, via Cannizzaro reaction, changes in the alkaline medium into 4-hydroxylaminobenzaldehyde, which reacts either with 4-nitrosobenzaldehyde or dimerises [41] giving 4,4'-diformylazoxybenzene as represented in the following scheme:



4-Nitrosobenzoic acid changes rapidly in the presence of alkali into 4,4'-dicarboxyazoxybenzene [42].

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