

ORGANIC SYNTHESIS
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Reduction of 4-Nitrosodiphenylamine with Sodium Hydroxy-
and Aminoalkanesulfinates

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Abstract—The kinetics of reduction of 4-nitrosodiphenylamine with sodium alkanesulfinates were studied, and the reaction mechanism was suggested.

Reduction of 4-nitrosodiphenylamine (NDPA) to 4-aminodiphenylamine (ADPA) is of great practical importance, since ADPA is an intermediate product in preparation of antioxidants. In particular, condensation of ADPA with acetone yields 4-isopropylaminodiphenylamine (commercial name Diafen FP) [1], which is thermal stabilizer for polyethylene, polystyrene, and synthetic rubber, inhibitor of tarring of motor fuel, and stabilizer of leaded gasolines. In recent years, derivatives of alkanesulfinic acids containing various substituents at the first carbon atom were found to be highly promising in reduction of organic nitro and nitroso compounds. The feature of these compounds is the presence of abnormally long C–S bond, which under certain conditions ruptures to form active intermediates having high reducing power: SO_2^{2-} and $\text{S}_2\text{O}_4^{2-}$ ions and SO_2^- radical anions [2]. The use of sodium hydroxymethylsulfinate as a reducing agent allows preparation of ADPA from NDPA in almost quantitative yield [3]. The mechanism of this reaction was thoroughly studied. It was shown that the initial substance can be reduced both with sulfoxylate anions and directly with hydroxymethanesulfinate molecules [4]. The absence of side reactions allows reliable determination of the rate constants of the stages involving decomposition of the reducing agent and the reaction of sulfoxylate anions with the oxidant. These parameters can be used for optimizing processes involving such reducing agents.

In this connection, it is appropriate to study the possibility of NDPA reduction with derivatives of alkanesulfinic acids with the aim to compare their reactivity and performance and also to elucidate the process mechanism.

EXPERIMENTAL

NDPA was prepared by threefold recrystallization of the commercial product from ethanol.

Sodium hydroxymethanesulfinate (SHMS), sodium hydroxyethanesulfinate (SHES), and sodium amino-methanesulfinate (SAMS) used as reducing agents were prepared by the procedures described in [5, 6]. The concentrations of their solutions were determined by iodometric titration [7].

NDPA was reduced directly in the colorimeter cell, which was placed into a temperature-controlled jacket connected to a UT-2 thermostat (the temperature was maintained with the accuracy of $\pm 0.5^\circ\text{C}$). The reaction rate was determined by measuring the optical density of the NDPA solution at $\lambda = 400$ nm, which corresponds to the absorption maximum in its electronic spectrum. It was found preliminarily that the reaction products and the reducing agent do not absorb light at this wavelength. The optical density was measured on a KFK-2 spectrophotometer equipped with an Shch-1516 digital dc voltmeter.

All kinetic measurements were carried out at more than thousand-fold excess of the reducing agent, which provides practically constant concentration of the reducing agent in the course of the experiment.

Preliminary experiments showed that the reaction of NDPA with SHMS in aqueous alkaline solution yields a compound that can be isolated by distillation in a vacuum at approximately 200°C . The melting point of this compound is $66\text{--}67^\circ\text{C}$, the half-wave reduction potential on a dropping mercury electrode $E_{1/2} = -0.23$ V (anodic wave), and the appearance of the product corresponds to published data for ADPA [8, 9].

To determine the stoichiometry of the reaction between SHMS and NDPA, we mixed the solutions of these compounds in 1 M aqueous NaOH. The resulting mixture was kept under argon at 73°C until decolorization, after which the SHMS content was determined iodometrically.

Table 1. Determination of the stoichiometric ratio of the reactants in reduction of NDPA with SHMS. Initial amount of NDPA 0.0147 mol

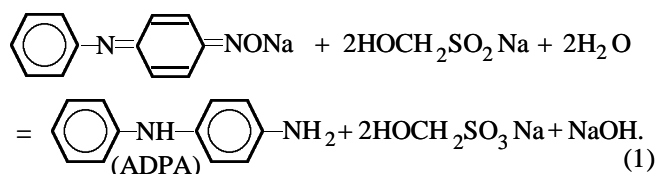
v_{SHMS}^*	ADPA obtained	v_{SHMS}^{**}	NDPA : SHMS*	Yield of ADPA, %
mole				
0.7178	0.0138	0.0799	1 : 1.9	94
0.1078	0.0145	0.0769	1 : 2.1	99
0.1051	0.0145	0.0742	1 : 2.1	99

* Before reaction.

** After reaction.

Table 1 shows that, under these conditions, ADPA is formed in quantitative yield, with the ratio of the reacted NDPA and SHMS being 1 : 2. Qualitative analysis showed that, in the course of reduction, sulfite sulfur is formed.

These results suggest the stoichiometric reaction equation



SHMS and SAMS are analogs of sodium hydroxymethanesulfinate [1]. Hence, there is good reason to believe that the reduction of NDPA with SHES and SAMS proceeds by a stoichiometric equation similar to Eq. (1).

The kinetic curves of NDPA reduction with various reducing agents are shown in Fig. 1. Contrary to re-

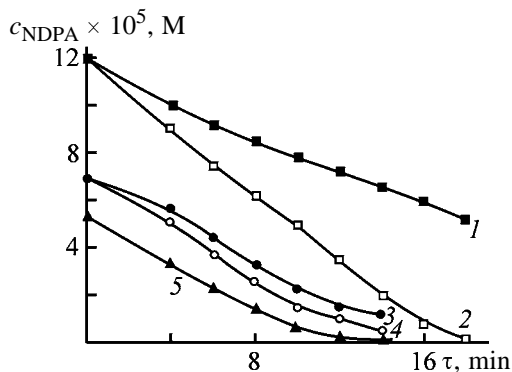
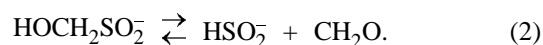


Fig. 1. Kinetic curves of NDPA reduction. (c_{NDPA}) NDPA concentration; (τ) time. (1, 2) SHMS, 309 K, $c_{\text{red}} = 0.5519$, $c_{\text{OH}^-} = 0.37$ M; (3, 4) SHES, 303 K, $c_{\text{red}} = 0.071$, $c_{\text{OH}^-} = 0.6$ M; (5) SAMS, 313 K, $c_{\text{red}} = 0.414$, $c_{\text{OH}^-} = 1.02$ M. (2, 4, 5) In the absence of additives; addition of the corresponding aldehyde, M: (1) 0.21 and (3) 0.02.

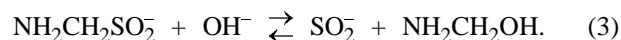
duction of 2-nitro-2'-hydroxy-5'-methylazobenzene (NAB) [10], the reaction between alkanesulfonates and NDPA proceeds without an induction period, with the reaction order with respect to the oxidant being fractional.

It is well known that reactions involving SHMS are inhibited by formaldehyde. This is due to the fact that the reducing species in some cases are not the molecules of the reducing agent but the products of their decomposition, sulfoxylate ions, formed by the reversible reaction [1]



Addition of formaldehyde and acetaldehyde inhibits the reaction in question (Fig. 1, curves 1 and 3), and at sufficiently high concentrations of the additives the reaction order with respect to NDPA becomes equal to 1 (Fig. 2a).

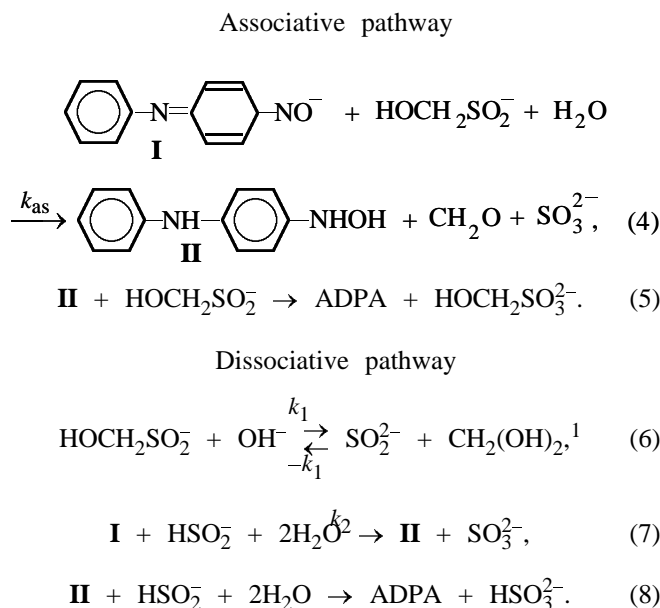
However, attempts to completely inhibit the reaction by adding aldehydes, as in the case of NAB and indigocarmin, failed [10, 11]. For example, in reduction of SHMS, the reaction rate on adding formaldehyde decreases by 60% at maximum, and with further addition of formaldehyde it remains constant. For SAMS, according to the equation of its decomposition with rupture of the C-S bond, aminomethanol should be an additive shifting the equilibrium to formation of nondissociated reducing agent molecules:



Aminomethanol does not exist in the free state [12]; therefore, it is impossible to carry out experiments with its addition to SAMS.

For all the reducing agents studied, the reaction rate varies in direct proportion to the concentration of the reducing agent (Fig. 2b) both in the presence of aldehydes and without them.

The above experimental data suggest that reduction of NDPA with derivatives of alkanesulfonic acids proceeds by two parallel pathways: direct reaction of NDPA with molecules of reducing agent (associative pathway) and reaction with the products of decomposition of reducing agent molecules, sulfoxylate anions (dissociative pathway). Based on the above and also published data [13], which note that the nitroso group is reduced in steps, we can propose the following reaction pattern (for SHMS as an example):



Since in the presence of aldehyde the reaction order with respect to the reducing agent and NDPA is equal to 1, we can assume that, in the associative pathway, reaction (4) will be the limiting stage and the subsequent fast stage (5) will not affect the overall rate of the process. The first reaction order with respect to the reducing agent in the absence of aldehyde additions and the inhibiting effect of the aldehydes suggest, by analogy with reduction of NAB, that in reduction by the dissociative pathway the limiting stage is cleavage of the reducing agent molecules (6). Applying the steady-state concentration method to stages (6) and (7), and considering the associative pathway, we obtain the kinetic equation

$$v_{ov} = -\frac{dc_{\text{NDPA}}}{dt} = v_{\text{dis}} + v_{\text{as}} = \frac{k_1 k_2 c_{\text{NDPA}} c_r c_{\text{OH}^-}}{k_{-1} c_a + k_2 c_{\text{NDPA}}} + k_{\text{as}} c_{\text{NDPA}} c_r \quad (9)$$

where v_{ov} , v_{dis} , and v_{as} are the overall reaction rate and the reaction rates by dissociative and associative pathways, respectively ($\text{mol l}^{-1} \text{s}^{-1}$); c_{NDPA} , c_{OH^-} , c_r , and c_a are concentrations of NDPA, hydroxide ions, reducing agent, and aldehyde (or aminomethanol), respectively (M); k_1 and k_{-1} are the rate constants of stage (6) ($\text{l mol}^{-1} \text{s}^{-1}$); k_2 and k_{as} are the rate constants of stages (7) and (4), respectively ($\text{l mol}^{-1} \text{s}^{-1}$).

Equation (6) can be experimentally verified for the reducing agents studied by analogy with reduction of NAB with SHMS [10].

¹ Methylene glycol is hydrated form of formaldehyde in alkali solution.

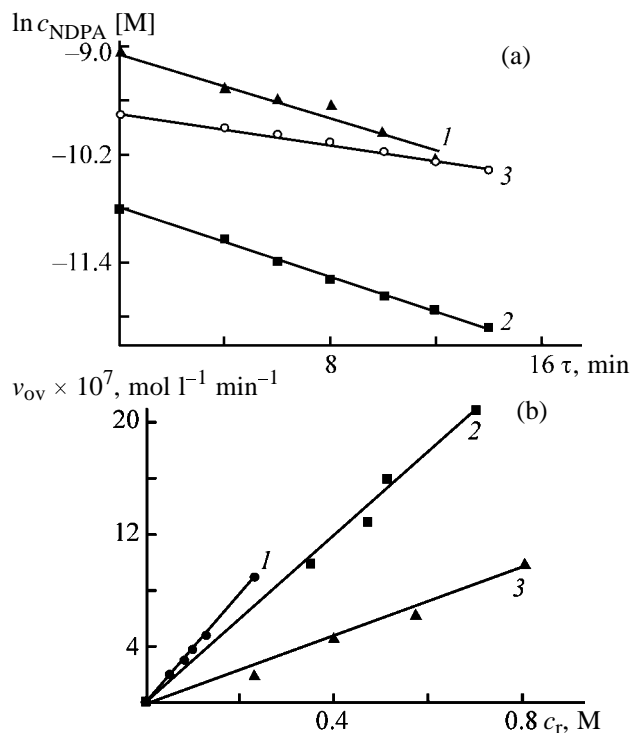


Fig. 2. Dependences of (a) $\ln c_{\text{NDPA}}$ on duration of NDPA reduction τ and (b) the reaction rate v_{ov} on concentrations of the reducing agents c_r : (a) (1) SHMS, 309 K, $c_r = 0.5519$, $c_{\text{OH}^-} = 0.37$, $c_a = 0.21$ M; (2) SHES, 303 K, $c_r = 0.0634$, $c_{\text{OH}^-} = 0.17$, $c_a = 0.013$ M; (3) SAMS, 303 K, $c_r = 0.4088$, $c_{\text{OH}^-} = 0.86$ M. (b) (1) SHES, 283 K, $c_{\text{OH}^-} = 0.5$, $c_{\text{NDPA}} = 2.5 \times 10^{-5}$, $c_a = 5 \times 10^{-5}$ M; (2) SAMS, 303 K, $c_{\text{OH}^-} = 0.75$, $c_{\text{NDPA}} = 2 \times 10^{-5}$; (3) SHMS, 308 K, $c_{\text{OH}^-} = 0.37$, $c_{\text{NDPA}} = 2.5 \times 10^{-5}$, $c_a = 0.21$ M.

For this purpose, based on the results of experiments performed at aldehyde concentrations sufficient to suppress pathways (6)–(8), we found k_{as} values (Table 2). Then, from the difference between the overall rate v_{ov} and the rate by the associative pathway v_{as} , we evaluated the reaction rates by the dissociative pathway v_{dis} , entering into the linear form of the kinetic equation

$$\frac{1}{v_{\text{dis}}} = A + \frac{B c_a}{c_{\text{NDPA}}}, \quad (10)$$

Table 2. Kinetic parameters of NDPA reduction with sodium alkanesulfonates

Reducing agent	$T = 283$ K		$T = 293$ K	
	k_{as}	k_1	k_{as}	k_1
	$\text{l mol}^{-1} \text{s}^{-1}$			
SHMS	9.5×10^{-4}	1.13×10^{-9}	1.3×10^{-3}	2.5×10^{-9}
SHES	1.13×10^{-3}	2.2×10^{-7}	5.5×10^{-3}	3.5×10^{-6}
SAMS	6.7×10^{-5}	6.7×10^{-9}	3.17×10^{-4}	1.43×10^{-8}

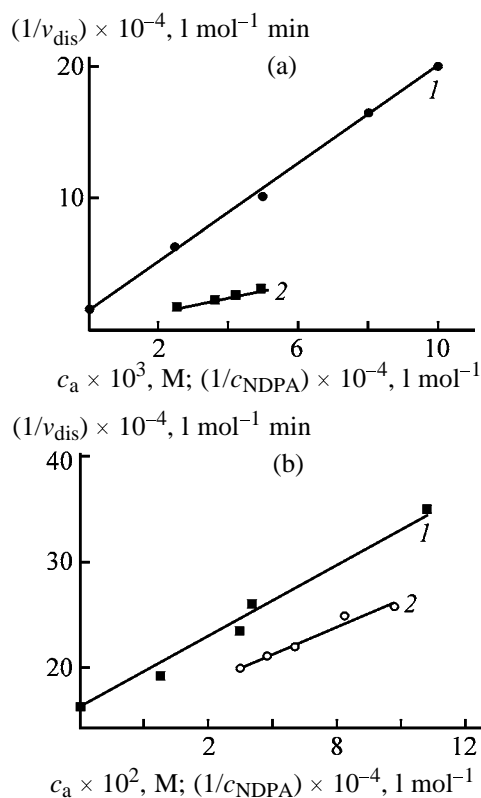


Fig. 3. Reciprocal reaction rate by dissociative pathway $1/v_{\text{dis}}$ as a function of (1) concentration of aldehydes c_a and (2) reciprocal concentration of NDPA $1/c_{\text{NDPA}}$: (a) SHES, 283 K; $c_r = 0.1064$, $c_{\text{OH}^-} = 1.8$; (1) $c_{\text{NDPA}} = 2.5 \times 10^{-5}$, (2) $c_a = 3.6 \times 10^{-3}$ M; (b) SHMS, 308 K; $c_r = 0.5519$, $c_{\text{OH}^-} = 0.37$; (1) $c_{\text{NDPA}} = 6 \times 10^{-5}$, (2) $c_a = 3.6 \times 10^{-2}$ M.

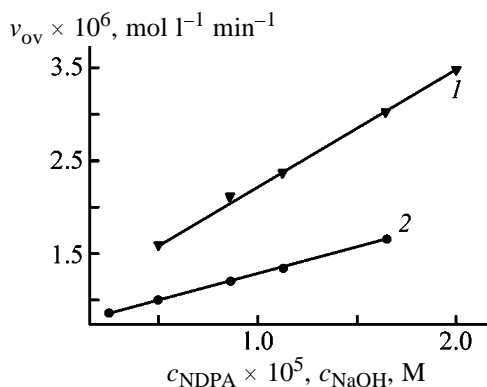


Fig. 4. Rate of NDPA reduction with HAMS v_{ov} as a function of (1) NDPA concentration c_{NDPA} and (2) concentration of hydroxide ions c_{OH^-} at 303 K. c_r (1) 0.468 and (2) 0.409; (1) $c_{\text{OH}^-} = 0.75$; (2) $c_{\text{NDPA}} = 2 \times 10^{-5}$ M.

where $A = 1/(k_1 c_r c_{\text{OH}^-})$, $B = k_1/(k_1 k_2 c_r c_{\text{OH}^-})$.

The linearity of the plots in the coordinates $1/v_{\text{dis}} - c_a$ at c_{NDPA} and $c_{\text{OH}^-} = \text{const}$ and $1/v_{\text{dis}} - 1/c_{\text{NDPA}}$ at c_a and $c_{\text{OH}^-} = \text{const}$ (Fig. 3) confirms the validity of Eq. (10).

Table 3. Kinetic parameters of NDPA reduction with SAMS

T, K	$v_{\text{ov}} = f(c_{\text{OH}^-})$		$v_{\text{ov}} = f(c_{\text{NDPA}})$	
	$k_{\text{as}} \times 10^3$	$k_1 \times 10^8$	$k_{\text{as}} \times 10^3$	$k_1 \times 10^8$
	$\text{l mol}^{-1} \text{ s}^{-1}$			
303	1.5 ± 0.3	2.3 ± 0.6	1.1 ± 0.2	4.0 ± 1.0
308	2.6 ± 0.3	4.0 ± 1.0	2.5 ± 0.5	4.0 ± 1.0
313	6.0 ± 1.0	6.0 ± 1.0	4.0 ± 0.8	6.0 ± 2.0

Table 4. Angular coefficients of dependences $v_{\text{ov}} = f(c_r)$ for NDPA reduction with SAMS

T, K	Angular coefficient	
	evaluation by Eq. (1)	experimental
303	3.02×10^{-6}	2.88×10^{-6}
308	6.14×10^{-6}	5.2×10^{-6}
313	7.01×10^{-6}	7.86×10^{-6}

From the initial ordinates of the above linear dependences, equal to the parameter A in Eq. (10), we evaluated the rate constants k_1 (Table 2).

As mentioned above, it is impossible to study how aminomethanol inhibits NDPA reduction with SAMS by shifting the equilibrium of decomposition of SAMS molecules by reaction (3). However, the experimental data obtained suggest that two-pathway scheme of reduction is realized in the case of this reducing agent also and it is possible to determine the same kinetic parameters that as in the case of SHMS and SHES.

The dependences of the rate of NDPA reduction with SAMS on the concentrations of NaOH and NDPA are shown in Fig. 4. The observed linear dependences with positive initial coordinates are in good agreement with the kinetic model proposed. Assuming that $k_{-1}c_a \ll k_2c_{\text{NDPA}}$, Eq. (9) is simplified:

$$v_{\text{ov}} = k_1 c_r c_{\text{OH}^-} + k_{\text{as}} c_{\text{NDPA}} c_r \quad (11)$$

The equation adequately describes the experimental data presented in Figs. 2 and 4.

The rate constants and activation energies were evaluated by least-squares treatment of these dependences for various concentrations of the reducing agent and sodium hydroxide and various temperatures (Table 3). Using the rate constants listed in Table 3,

we evaluated the angular coefficient of the dependence $v_{\text{ov}} = f(c_r)$ by Eq. (11) and compared with the experimental data (Fig. 2b) (Table 4). Satisfactory agreement of these results additionally confirms the adequacy of the proposed kinetic model. From the temperature dependences of the rate constants listed in Table 3, we evaluated the activation energies for the associative and dissociative pathways to be 106 ± 10 and 53 ± 2 kJ mol⁻¹, respectively.

It should be noted in conclusion that the found rate constants k_1 (Table 2) characterize the ease of the rupture of the C–S bond in alkanesulfinate molecule. From the above data, the reducing agents can be ranked in the following order with respect to stability: SHES < SAMS < SHMS.

CONCLUSION

Based on the kinetic data for reduction of 4-nitrosodiphenylamine with sodium hydroxymethanesulfinate, sodium hydroxyethanesulfinate, and sodium aminomethanesulfinate, the kinetic equations were obtained. These equations suggest that the reaction proceeds by two parallel pathways: direct reaction of the substrate with reducing agent molecule (associative pathway) and reaction with the product of reducing agent decomposition, sulfoxylate anion (dissociative pathway).

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