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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Reduction of 4,4'-Dinitrostilbene-2,2'-disulfonic Acid with Hydrogen on Raney Nickel

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Abstract—Reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid with hydrogen in aqueous solution on Raney nickel yields a trisazo compound identical to Direct Yellow K dye.

In syntheses of some dyes and optical whitening agents, 4,4'-diaminostilbene-2,2'-disulfonic acid (DAS) is widely used as the diazo component. At present, this acid is prepared from 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNS) by Bechaump reduction [1]. The drawbacks of this process are large amounts of wastewater, the necessity of utilizing the iron slime, and labor-consuming isolation of the target product; they make the process environmentally and economically unacceptable. Heterogeneous-catalytic reduction of DNS with hydrogen in the liquid phase (see scheme) is more efficient and economically feasible. However, this process is accompanied by formation of by-products and intermediates decreasing the yield and quality of DAS. The scheme of catalytic reduction of DNS suggested by Bizhanov and Zhubanov [2] does not

reflect all the transformations that DNS undergoes under conditions of catalytic reduction. Bizhanov and Zhubanov proved the possibility of hydrogenation of the C=C double bond in the stilbene moiety with the formation of 4,4'-diaminodibenzyl-2,2'-disulfonic acid (DADB) and *p*-aminotoluenesulfonic acid; they also noted formation in solution of diazo compounds and unidentified unstable colored products. Formation of an unidentified red product in reduction of DNS was noted in [3, 4]. It was suggested that the compound imparting the red color to the reaction mixture in the course of DNS reduction contains an azoxy group [4]. At the same time, DAS can be prepared by hydrogenation of a mixture of azo dyes containing as major component the trisazoxy dye Direct Yellow K (DYK) of the following structure [7]:



According to the Haber–Lukashevich–Shmonina scheme, nitro compounds are reduced in steps, with the products of incomplete hydrogenation of the NO_2 group being capable to react with each other to form azoxy compounds [6, 7]. Therefore, presumably, heterogeneous-catalytic reduction of DNS can yield a product identical to DYK, imparting the red color to the catalyzate and the cream color to the isolated target product.

Papers concerning the DAS production process discuss the influence of various process conditions on the product quality. This influence cannot be understood without data on intermediates and by-products. Therefore, the goal of this work was to prepare and study intermediates and by-products arising in catalytic reduction of DNS. The results would allow us to suggest a more detailed scheme of DNS reduction with hydrogen on Raney nickel and to find conditions for preparing the purest target product. Scheme of heterogeneous-catalytic reduction of DNS



where DNSS is 4,4'-dinitrosostilbene-2,2'-disulfonic acid and DHAS is 4,4'-di(hydroxylamino)stilbene-2,2'-disulfonic acid.

EXPERIMENTAL

Catalytic reduction of DNS with hydrogen was performed at atmospheric pressure in a Vishnevskii apparatus with vigorous stirring of the liquid phase. Raney nickel was prepared by leaching nickel-aluminum alloy (1:1 by weight) with a 25% NaOH solution. Crude DNS was purified by double recrystallization, which yielded fine yellow needle-like crystals soluble in water and dimethyl sulfoxide. The intermediate, hereinafter denoted as X, was prepared by reduction of DNS. A reaction vessel was charged with 2 g of the catalyst washed to remove NaOH and with 100 ml of water. The vessel was purged with hydrogen, after which the catalyst was saturated with hydrogen at stirring (1000 rpm) for an additional 10 min. Then 7 g of DNS was added, and reduction was performed at 303 K for 5 min with stirring (4000 rpm). Under these conditions, the reduction yielded a red solution, which was filtered to remove the catalyst and evaporated. The residue was recrystallized from DMF. A red powder was obtained, soluble in water and DMF. Separate experiments showed that intermediate X can be reduced to DAS in the presence of Raney nickel.

The target product, DAS, was prepared by reduction of DNS (1 g) in citrate–phosphate buffer solution (pH 9.5) at 303 K on Raney nickel (1 g). The crude product was recrystallized from water. The resulting flesh-colored needle-shaped crystals were soluble in aqueous alkali. DADB was prepared by hydrogenation of DAS (1 g) in aqueous solution on Raney nickel and isolated by acidification with HCl to pH 2.35. The product was a white amorphous powder. DYK was prepared according to [5] from nitrotoluenesulfonic acid and purified by recrystallization from DMF. The product was a red powder soluble in water and DMF. All the products were sulfo derivatives; they decomposed without melting above 300°C.

To determine the structure of intermediate X, all the above substances were studied by IR and UV spectroscopy. For DYK and product X, we also recorded the ¹H NMR spectra and performed elemental analysis. The UV spectra were taken on an SF-46 spectrophotometer in the wavelength range 250– 500 nm in aqueous solution (cell thickness 1 cm). The IR spectra were taken on a Specord M80/M85 spectrophotometer in the frequency range 4000–200 cm⁻¹ using the KBr technique (0.002–0.0024 g of substance per 0.3 g of KBr, pressing at 6000–1000 atm with continuous evacuation to 10^{-3} mm Hg). The ¹H NMR spectra were taken on a Bruker AMX spectrometer (400.13 MHz, DMSO-d₆) relatve to internal TMS.

The C=C double bond was detected by iodination, and the amino group, by diazotization. Elemental analysis was performed by the standard procedure [8].

The UV spectra of DNS, DAS, DADB, product X, and DYK are shown in Fig. 1. The spectra of DNS

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Com- pound	v, cm ⁻¹								
	-CH=CH-	C=C (arom.)	C–H (arom.)	CH ₂ - (aliph.)	-NO ₂	-NH ₂	–SO ₃ H		
DNS	1664 vs	1472, 1484, 1576	968, 976	_	752, 848, 876 1348, 1520– 1568	_	628, 1080, 1296		
DAS	1664	1496, 1568, 1576, 1584, 1608	912, 976	_	_	640, 660, 1256 1496, 3312–3400 3512	628, 1080, 1280		
DADB	_	1436, 1508, 1584, 1620	968, 976	2624, 2712, 2960	_	672, 704, 796 908, 1272, 1508 1508, 3280, 3448	624, 1088, 1272		
DYK	1664 vs	1472, 1568	976	_	_	_	624, 1128, 1288		
Х	1664 vs	1456, 1568	968, 976	-	-	_	624, 1128, 1288		

Table 1. IR spectra of DNS and its reduction products

and DAS differ insignificantly. The only absorption maximum in the spectrum of DNS (350 nm) corresponds to the π - π * transition with the electron transfer to the NO₂ group [6]. In the UV spectrum of DAS, there is a maximum at λ = 340 nm, characteristic of aromatic amines [9]. Absorption in the visible range is insignificant. DADB has no absorption maxima in the examined range. The spectra of product X and DYK appeared to be virtually identical. The maximum at about 440 nm is assigned to the n- π * transition.

The IR spectra of all the compounds listed in Table 1 contain bands assignable to vibrations of the sulfo group and aromatic CH group, skeleton vibrations of benzene rings, and out-of-plane bending vibrations of the C–H bonds in benzene rings. The spectrum of DNS also contains the NO₂ vibration bands, and the spectra of DAS and DADB, the vibration



Fig. 1. UV absorption spectra of (1) DNS, (2) DAS, (3) DADB, (4) product X, and (5) DYK. (ε) Extinction coefficient and (λ) wavelength.

bands of the NH₂ group. Because DADB contains no -CH=CH- bond, in the spectrum of this compound the band at 1664 cm⁻¹ is lacking, but bands assignable to stretching vibrations of the aliphatic CH₂ group are observed, which are absent in the spectra of the other substances.

The spectra of product X and DYK contain a whole set of bands confirming the presence of the stilbene double bond, benzene rings, and sulfo group. A distinctive feature of the spectra of X and DYK, as compared to those of the other compounds, is the presence of a strong band at 1300-1304 cm⁻¹ belonging to the azoxy group. The fine structure of the spectra of X and DYK in the range 1300-900 cm⁻¹ is slightly different, which may be due to partial hydrogenation of double bonds between the benzene rings in the course of catalytic reduction. In other respects, the spectra of DYK and product X virtually coincide.

Comparison of the chemical shifts in the ¹H NMR spectra of product X and DYK (Table 2) shows that all the major fragments in these substances coincide. Insignificant differences are due to the presence of the aliphatic CH_2 - CH_2 bond in product X.

Both X and DYK are neither iodinated nor diazotized. Elemental composition of X, found, %: C 42.3; N 7.2; H 2.8. Calculated for DYK, %: C 42.2; N 7.0; H 2.5. The difference between the spectra of DYK and product X may be due to simultaneous transformations of intermediates with different extents of reduction under the conditions of the heterogeneous-catalytic reaction. As a result of the reactions suggested in

Compound	¹ H NMR spectrum, δ, ppm								
	H ¹ (arom.)	H ² (arom.)	H ³ (arom.)	-CH=CH-	SO ₃ H	-CH ₂ -CH ₂ -			
DYK X	8.669 (8H) 8.681 d (8H)	8.165 d (8H) 8.166 d (8H)	6.832 d (8H) 6.796 d (8H)	5.390 (8H) 5.375 (8H)	2.611 d (8H) 2.611 d (8H)	2.337 s			

Table 2. ¹H NMR spectra of DYK and product X

[7], product X contains impurities of azo coupling products with similar properties. Apparently, reduction of DNS occurs via azo coupling of product X with other reaction participants. Thus, heterogeneous-catalytic reduction of DNS in aqueous solution follows a complex pattern involving much more species than it was suggested earlier [2].

We plotted a calibration chart to determine the concentration of X from the optical density of its solutions at 440 nm and, using these data, examined how the concentration of X in hydrogenation products varies with time in the course of DNS reduction (Figs. 2a, 2b). The concentration of X passed through a maximum in the initial period of the reaction. The maximal concentration of X depended on the weight ratio of DNS to the catalyst (the lower this ratio, the lower the maximal concentration of X was attained at pH 9.5–9.7. At this pH the reaction was also the most



Fig. 2. Concentration of product X *C* as a function of time τ in (a) aqueous and (b) phosphate buffer solutions. 303 K; 0.5 g of DNS. (a) Catalyst weight, g: (1) 0.4, (2) 0.5, (3) 1.0, and (4) 2.0. (b) Catalyst weight 1 g; pH: (1) 5.64, (2) 9.68, and (3) 11.00.

selective with respect to hydrogenation of the NO_2 group to form DAS (the stilbene double bond was not involved). Therefore, formation of X can be considered as a condition for selective formation of the target product.

We have shown previously [10] that at low weight ratios of DNS to the catalyst the DNS reduction occurs with an induction period. Comparison of the induction period to the time in which the concentration of X reaches a maximum shows that a low rate of hydrogen uptake is associated with formation of this intermediate. Apparently, rapidly forming product X blocks the catalyst surface and prevents further reduction. This is accompanied by partial reduction of X with the metal of the catalyst, primarily with residual aluminum.

The homogeneous stages of coupling of X with reactants play a major role under conditions when the amount of hydrogen on the catalyst surface is insufficient (Figs. 2a, 2b, curves 1), i.e., at large DNS loads and deficiency of the catalyst. To improve the quality of DAS, such unfavorable conditions should be avoided.

CONCLUSIONS

(1) An intermediate of reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid in aqueous solution on Raney nickel was detected and studied; it is identical to Direct Yellow K trisazo dye.

(2) Formation of this intermediate explains the kinetic features of reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid and is the cause of the reaction deceleration. Incomplete reduction of this product results in decreased process selectivity.

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