Kinetics and Mechanism of Diphenylamine Synthesis by the Condensation of Aniline with Oxygen-Containing Compounds

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Abstract—The condensation of aniline and cyclohexanol (cyclohexanone) yielding intermediates and the subsequent dehydrogenation of these intermediates into diphenylamine have been studied. The mechanism of diphenylamine synthesis is substantiated. The kinetics of diphenylamine synthesis from aniline and cyclohexanol over a NiSnMg catalyst has been studied. A kinetic model in terms of the conversion of strongly chemisorbed species has been developed. The rate constants of diphenylamine synthesis at 260–300°C have been determined, which are consistent with the observed regularities. The kinetic model can be used in the determination of optimal synthetic conditions and in the design of a reactor for diphenylamine synthesis from aniline and cyclohexanol. Conditions have been found under which diphenylamine synthesis occurs at a high rate of up to 1 kg/(l h), with high selectivity, and with a high yield of up to 95%.

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Diphenylamine (DPA) and its derivatives are among the most important stabilizers and/or antioxidants for fuels [1, 2], oils [3, 4], and various polymers. In particular, synthetic rubber plants use DPA as an effective antioxidant for stabilization of plastics, elastomers, and latexes in the manufacture of tires and other rubberware [5–7].

Two DPA synthesis schemes have been suggested, namely, aniline (An) autocondensation over acid catalysts [8, 9] and aniline condensation with oxygen-containing compounds, such as phenol and cyclohexanone (CH) [10–12].

The kinetics of DPA synthesis was not studied. The main problems of DPA synthesis by the condensation of aniline with cyclohexanone are the deactivation of the catalyst during the process and the decrease in the desired-product selectivity caused by C–N bond hydrogenolysis.

We have established that catalyst deactivation is mainly due to resins resulting from the condensation of initial cyclohexanone with the intermediate compound *N*-cyclohexylideneaniline (CDA), a Schiff base. The main factor in the DPA selectivity of the process is the cyclohexanone/aniline molar ratio. Indeed, the DPA yield decreases as this ratio is increased because of the conversion of DPA into triphenylamine. Therefore, an excess of aniline and cyclohexanol as the oxygen-containing reagent should be employed in order to enhance the DPA selectivity and the stability of the catalyst. Thus, for stable DPA synthesis from cyclohexanone (cyclohexanol) and aniline, the catalyst should be very

active in the condensation and dehydrogenation reactions of the cyclohexane ring of the cyclohexylaniline (CHA) and CDA molecules. Moreover, the hydrogenolysis of the C–N bond should be suppressed.

In order to optimize DPA synthesis and to be able to control the process, it is necessary to elucidate the mechanism of the synthesis and to develop an appropriate kinetic model.

EXPERIMENTAL

The condensation of cyclohexanol with aniline was studied in the temperature range 530–590 K at atmospheric pressure in a flow quartz reactor 12 mm in diameter with a 3- to 10-ml fixed catalyst bed.

Reagent-grade aniline, cyclohexanol, and cyclohexanone were distilled immediately before the synthesis. The physical constants of these reagents were in agreement with reference data. Cyclohexylaniline was obtained by the condensation of cyclohexanol and aniline (1 : 1) over a copper–zinc catalyst according to a standard procedure [13]. The Schiff base (CDA) was synthesized by the condensation of cyclohexanone and aniline (1 : 1.2) in the presence of 0.5% HCl at 150–160°C followed by the isolation of the fraction boiling at 156–157°C (30 Torr). According to GC–MS data, CHA was 99% pure (the major impurity was aniline). The ^{1}H NMR spectra (CCl$_4$) of synthesized CHA and

Table 1. Influence of temperature and contact time on the product composition for the condensation of cyclohexanol and aniline over the NiSnMg catalyst

T, K	$\tau \times 10^2$, l h mol^{-1}	Concentration, wt %					
		cyclohexanol + cyclohexanone	phenol	aniline	CHA	CDA	DPA
573	0.850	2.6	0.1	64	12.3	1.05	20
	1.267	1.8	0.15	59	9.0	0.85	29.1
	2.130	0.3	0.15	61.3	0.75	0.50	37
	2.846	0.15	0.2	58.2	0.30	0.15	41
	4.016	Trace	0.15	56.8	0	0	43
553	1.260	2.8	Trace	59.2	18.3	0.6	19.1
	1.990	2.2	0.2	58.7	10.7	1.2	27
	4.560	0.3	0.1	58.5	3.3	0.3	37.5
	6.430	0	0.2	58.6	2.6	0.1	38.5
533	1.250	7.7	0	64.6	15.4	1.2	11
	2.000	2.6	0	60.2	18.7	2.5	16
	3.700	2.3	0	61.2	10.2	0.8	25.5
	5.700	1.5	Trace	60.8	6.8	0.4	30.5

CGD are in agreement with the spectra known from the literature [14].

The following bottled gases were used: hydrogen (electrolytic grade), helium (special-purity grade), argon (special-purity grade), and nitrogen (pure grade).

All catalysts were prepared by modifying the commercial catalyst GM-3 (kieselguhr-supported nickel). Initial GM-3 (1–2 mm particles) was impregnated with an ethanolic solution of tin(II) and magnesium chlorides. The catalyst used in the synthesis contained ~50 wt % Ni and ~3 wt % (Sn + Mg) supported on kieselguhr. The specific surface area of nickel in the NiSnMg catalyst was 22 m^2/g [15].

The reaction mixture in the DPA synthesis was analyzed by GLC (flame-ionization detector, 6000 mm (3 mm i.d.) column packed with OV-225/Chromaton N Super, programmed heating from 105 to 210°C). The molar ratios of reagents and additions were the following: aniline/Cl, 6 : 1 to 3 : 1; H$_2$/cyclohexanol, 0.2–2; H$_2$O/cyclohexanol 1–5. Toluene or a toluene–nitrobenzene mixture was employed as the inert diluent. The apparent contact time (τ) was varied between 0.008 and 0.05 (l h)/mol by adding nitrogen (special-purity grade) to the reaction mixture. The concentration of the reagents in the mixture did not exceed 8 mol %. Since aniline was present in threefold excess, the real increase in the volume of the reaction mixture due to hydrogen

evolution did not exceed 4%, and it was not taken into consideration in further calculations.

It was demonstrated that the reaction is kinetically controlled when the catalyst particle size is <2 mm and the mixture flow velocity is >4 cm/s.

RESULTS AND DISCUSSION

The most important data characterizing cyclohexanol–aniline condensation over the NiSnMg catalyst at various temperatures and contact times are listed in Table 1.

It is clear from the data presented in Table 1 that the interaction between cyclohexanol and aniline in the presence of the catalyst yields a mixture consisting of DPA; CHA; CDA; and light by-products, such as phenol and cyclohexanone, whose total amount does not exceed 10 rel. %. The triphenylamine concentration in the mixtures containing excess of aniline did not exceed 1%; however, DPA condensation with cyclohexanol cannot be neglected when cyclohexanol is in excess.

Note that CHA is the main reaction product second to DPA. The concentrations of CDA (at 533 and 553 K) and CHA (at 533 K) pass through a maximum as the contact time is extended. This is typical of intermediate compounds. Under these conditions, the conversion of the initial reactants into the intermediates CHA and

Table 2. Cyclohexylaniline and N-cyclohexylideneaniline conversion over NiSnMg at 300°C and a feed rate of 0.9 kg l^{-1} h^{-1} (the diluent is toluene (50 wt %))

Time, h	CHA conversion, %	CDA conversion, %	Yield, %				
			DPA	aniline	BP*	CHA	CDA
3	100	–	80	18.7	0	0	Trace
7	99	–	87.8	11.2	0	1	Trace
14	98	–	82.6	15.3	0.2	2	Trace
3	–	100	80.3	13.3	6.4	0	0
9	–	100	88	9.6	2.0	0.4	0
12	–	100	87.2	9.9	1.8	1.1	0

* BP = by-products (benzene + cyclohexane).

CDA proceeds substantially more rapidly than the formation of DPA. Therefore, the kinetic experiment can be carried out only in an integral reactor.

Next, the effects of hydrogen, water, cyclohexanone, toluene, and nitrobenzene were studied. It was found that toluene does not affect the DPA synthesis; i.e., it is an inert diluent. Hydrogen admixtures (H_2/cyclohexanol = 0.2–2) do not significantly affect the synthesis, except for $\tau > 0.04$ l h mol^{-1}, when addition of hydrogen causes a decrease in the DPA yield. Introduction of water into the reaction mixture results in a significant reversible slowdown of DPA synthesis. The CDA concentration in the products decreases most greatly. This fact is consistent with the properties of the Schiff bases [10, 16, 17]. The use of the polar solvent nitrobenzene suppresses DPA synthesis completely and irreversibly.

All components of the reaction mixture (amines, cyclohexanol, cyclohexanone, phenol, etc.) containing reactive functional groups are strongly chemisorbed on the catalyst surface and then transform into the desired products or by-products. The addition of nitrobenzene, a polar compound, completely suppresses the synthesis by blocking the active catalyst surface. Therefore, the Schiff base does not undergo thermolysis to DPA under the conditions examined.
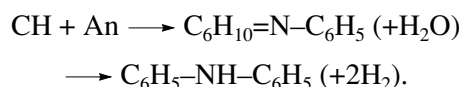
It was established by experiments carried out at different degrees of dilution of the reaction mixture with toluene that the initial rate of DPA formation does not depend on the partial pressures of the reactants. Hence, the dehydrogenation reaction is zero-order with respect to both cyclohexanol and aniline.

Addition of DPA (up to 20%) to the reaction mixture causes a small decrease in the DPA formation rate, and this effect weakens as the temperature is raised. How-ever, as the contact time is extended, DPA formation slows down because of hydrogenation/hydrogenolysis reactions involving the hydrogen produced.

Mechanism of DPA Synthesis by the Dehydrocondensation of Oxygen-Containing Cyclohexane Derivatives with Aniline

DPA synthesis from oxygen-containing cyclohexane derivatives is believed to proceed via intermediate CDA formation followed by complete dehydrogenation:

$$CH + An \longrightarrow C_6H_{10}=N-C_6H_5 \ (+H_2O)$$
$$\longrightarrow C_6H_5-NH-C_6H_5 \ (+2H_2).$$

The transformations of the possible intermediate compounds, namely, CHA and CDA, were studied to elucidate the formation route of the reaction products and to substantiate the general scheme of the reaction mechanism.

As is clear from Table 2, the by-products CHA, aniline, cyclohexane, and benzene result from CDA dehydrogenation along with DPA, the desired product. The presence of CHA in the reaction mixture is due to the hydrogenation of CDA by hydrogen involved in the reaction ($C_6H_{10}=N-C_6H_5 + H_2 \longrightarrow C_6H_5-NH-C_6H_{11}$), and the hydrocarbons result from C–N bond hydrogenolysis in CDA. These reactions are very undesirable because CDA and the intermediate hydrogenolysis products are capable of coking rapidly under the synthesis conditions. A similar situation is observed for cyclohexylamine dehydrogenation.

When CHA or CDA is employed instead of the initial cyclohexanol–aniline mixture, DPA synthesis proceeds under similar conditions. The product composition is nearly the same in these three systems. Therefore, the CHA formation and dehydrogenation steps are fast and reversible and CHA and CDA are indeed inter-
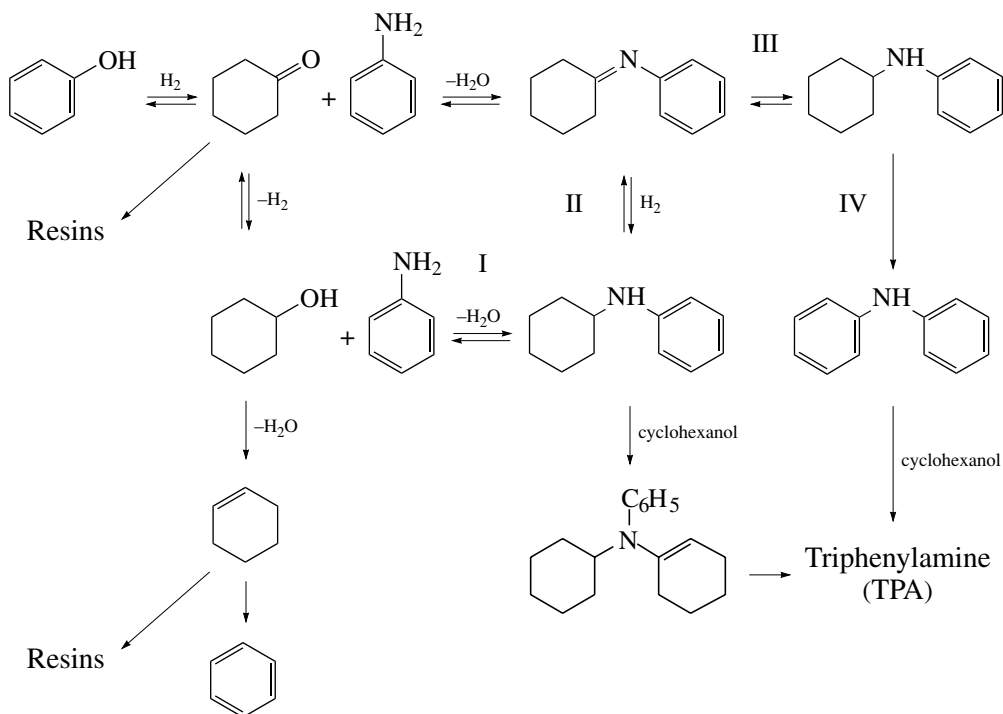
mediate products of DPA synthesis. Thus, the following reactions occur in DPA synthesis under the conditions examined:

(1) cyclohexanol–aniline condensation yielding CHA;

(2) dehydrogenation of the CHA ring yielding a Schiff base (CDA);

(3) CDA dehydrogenation yielding DPA;

(4) CDA hydrolysis yielding aniline, cyclohexanone, and by-products;

(5) DPA hydrogenation yielding CDA and CHA.

Thus, the preliminary investigation suggests the following scheme of aniline and cyclohexanol (or cyclohexanone) conversions.

Scheme.

Kinetic Model of Diphenylamine Synthesis from Aniline and Cyclohexanol

The effects of temperature and contact time on the yield of the desired product (DPA) are illustrated in Fig. 1. The DPA yield (Y) increases up to its maximum as τ is increased. As the temperature is raised, the maximum yield increases and is reached at progressively smaller τ values. Under the given experimental conditions, the cyclohexanol conversion (x) is above 95% and the qualitative composition of the reaction mixture is invariable.

The peak in the $Y(\tau)$ curve and the decrease of Y at larger τ values are due to the reverse hydrogenation of DPA with adsorbed hydrogen, whose concentration is virtually independent of whether hydrogen is added to the reaction mixture.

According to the concept of tightly chemisorbed species, the coverage of the catalyst surface is governed by adsorption-assisted desorption [18, 19]. This approach was employed to analyze the kinetics of DPA
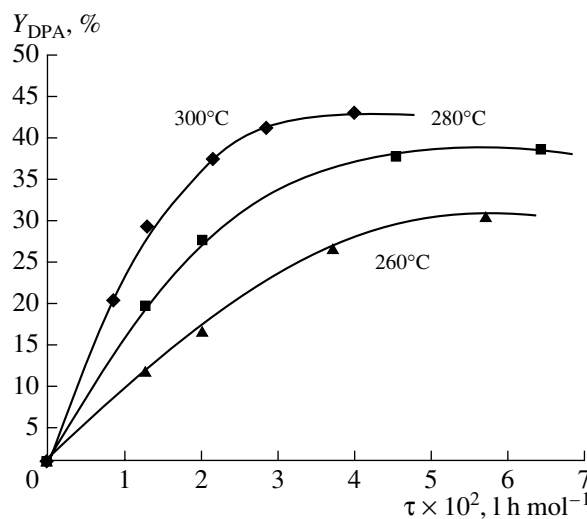

Fig. 1 Dependence of the DPA yield on the contact time for aniline/cyclohexanol mixture (3 : 1) over the NiSnMg catalyst at various temperatures.
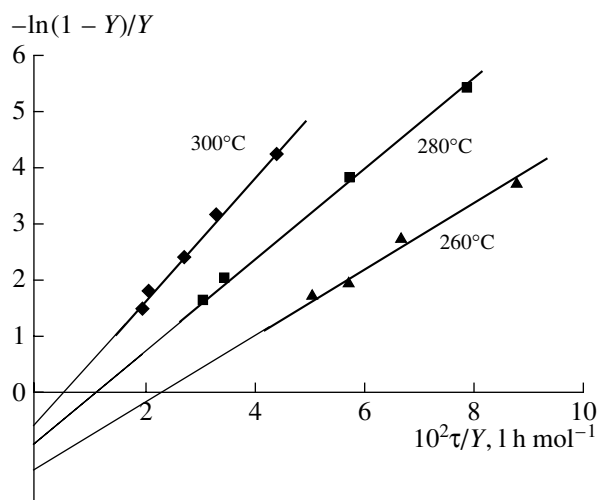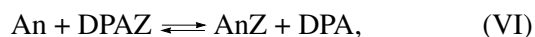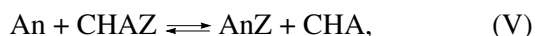
Fig. 2 Verification of Wq. (5) against the observed kinetics of DPA synthesis from aniline and cyclohexanol (NiSnMg catalyst).

synthesis and other complicated heterogeneous catalytic reactions [20, 21].

According to the scheme, the DPA accumulation rate is given by

$$r_{DPA} = k_4\theta_{CDA} - k_{-4}\theta_{DPA}\theta_H, \qquad (1)$$

where θ_j is the concentration of a reactant on the catalyst surface. It can be assumed that $k_{-4}\theta_H = k$, since hydrogen introduced into the gas phase does not affect the kinetics of the process. The CDA concentration ($\theta_{CDA} = K_2K_3\theta_{CHA} = K\theta_{CHA}$) is determined by the equilibrium between steps (II) and (III) in the scheme, and the CHA and DPA coverages of the surface are determined by the reversible adsorption-assisted desorption reactions:

$$An + CHAZ \rightleftharpoons AnZ + CHA, \qquad (V)$$

$$An + DPAZ \rightleftharpoons AnZ + DPA, \qquad (VI)$$

where Z is an active surface site and An = aniline,

$$\theta_{CHA} = \frac{\theta_A C_{CHA}}{K_5 C_{An}}, \qquad (2)$$

$$\theta_{DPA} = \frac{\theta_A C_{DPA}}{K_6 C_{An}}. \qquad (3)$$

Taking into consideration the composition of the reaction mixture (aniline/cyclohexanol = 3) and the balance equation for the species on the catalyst surface, the DPA formation rate can be expressed as follows:

$$r_{DPA} = \frac{dY}{4d\tau} = \frac{k_4K(1 - Y) - k(K_5/K_6)Y}{1 + 3K_5 + (K_5/K_6 - 1 - K_5)Y}, \qquad (4)$$

where Y is the DPA yield in terms of cyclohexanol passed ($Y = 0$ at $\tau = 0$), K_i is the equilibrium constant of the ith step of the reaction stage, and τ is the apparent contact time (l h mol^{-1}).

The integral of Eq. (4) is

$$-\ln(1 - a_3Y)/Y = \frac{a_2}{a_3(a_1a_3 + a_2)} + \frac{4k_4K\tau}{(a_1a_3 + a_2)Y}, \qquad (5)$$

where a_i is the following group of constants:

$$a_1 = 1 + 3K_5, \quad a_2 = K_5/K_6 - 1 - K_5,$$
$$\text{and} \quad a_3 = 1 + kK_5/(k_3KK_6). \qquad (6)$$

The experimental data in the coordinates of Eq. (5) are presented in Fig. 2. Clearly, the experimental points fall on straight lines, making it possible to estimate the group constants presented in Table 3.

The adequacy of the model to the process is clear from the data listed in Table 4, which show that the experimental and calculated data are in a good agreement.

The temperature dependence of the constants presented in Table 3 is described by the Arrhenius equation. The sum of the activation energy of step (IV) and the enthalpy of the equilibrium steps (II) and (III) are $E_4 - Q_2 - Q_3 = 87$ kJ/mol. The enthalpy of step (V) is $Q_5 = -155$ kJ/mol. The heat of step (VI) is apparently close to zero. The large negative value of Q_5 is apparently due to the high catalyst surface affinity of CHA in comparison with aniline. This assumption is consistent with the basicities of these amines [16].

The energetic parameters determined are in agreement with the assumptions underlying the model and are consistent with experimental data. Thus, the kinetic model is adequate and can be employed in the design of commercial reactors for diphenylamine synthesis from aniline and cyclohexanol.

Table 3. Constants of the kinetic model of DPA synthesis over the NiSnMg catalyst

T, K	k_4K, mol (l h)$^{-1}$	$-A$	$-a_2$	a_3	K_5	K_6
533	7.75	1.2	0.93	1.481	0.02	0.22
553	15.6	0.7	0.67	1.193	0.073	0.18
573	30.3	0.4	0.5	0.883	0.18	0.26

Table 4. Comparison of the experimental data and the data calculations using Eq. (5)

T, °C	Experiment		Calculation	
	$\tau \times 10^2$, l h mol^{-1}	Y, mole fractions	Y, mole fractions	$\tau \times 10^2$, l h mol^{-1}
300	0.85	0.433	0.4	0.693
	1.267	0.618	0.53	1.0137
	–	–	0.65	1.404
	–	–	0.75	1.8707
	2.13	0.783	0.83	2.477
	2.846	0.865	0.86	2.843
	4.016	0.906	0.88	3.1914
280	–	–	0.1	0.27
	1.26	0.412	0.35	1.008
	–	–	0.53	1.7638
	1.99	0.577	0.63	2.3638
	–	–	0.7	2.961
	4.56	0.793	0.75	3.610
	6.43	0.814	0.8	4.824
260	1.25	0.247	0.28	1.4885
	2.0	0.35	0.4	2.323
	3.7	0.556	0.5	3.221
	–	–	0.6	4.5582
	5.7	0.649	0.68	6.879

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