KINETICS OF HYDROGENATION AMINATION OF 2-PROPANOL WITH ANILINE ON A COPPER–CHROMIUM CATALYST

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The kinetics of hydrogenation amination of alcohols in the liquid phase were studied in the presence of a copper(II)–chromium(III) catalyst, 2-propanol and aniline were used as the models. In addition to the kinetic investigation of the model reaction as a whole, the partial reaction steps — dehydrogenation of 2-propanol and condensation of aniline with acetone — were also examined. It was proved that, in the reaction of aniline with 2-propanol on the copper-chromium catalyst, the formation of acetone is equilibrium-controlled. The overall rate of amination of 2-propanol with aniline is determined by both the condensation of acetone with aniline and the hydrogenation of the ketimine intermediate. The amination is accelerated by addition of aluminosilicate to the copper–chromium catalyst, which confirms that the ketimine concentration is not equilibrium-controlled.

The reactions of alcohols or other hydroxy compounds (glycols, alkanolamines) with ammonia represent the most widespread procedure for the preparation of amines. Similarly, primary amines react with alcohols to give secondary amines which then produce tertiary amines. The reaction of ammonia or amines with alcohols can be catalyzed by various types of catalysts: strong mineral acids, solid oxide catalysts, and hydrogenation-dehydrogenation catalysts.

Hydrogenation-dehydrogenation catalysts are being increasingly used in industrial processes. Thus metal catalysts are used in the production of the lower alkylamines (except methylamines), to produce cyclohexylamine (from cyclohexanol), and also in the alkylations of aniline at its nitrogen atom. With regard to the newer processes for the production of aliphatic higher alcohols, the so-called fatty amines have also recently begun to be produced by the amination of alcohols. In the production of 1,2-ethanediamine and morpholine, too, the amination of the hydroxy compounds (ethanolamine, diethylene glycol) replaces the older ways of manufacture. As compared with the preparation of amines from aldehydes or ketones the amination of alcohols is more convenient, because the prices of the alcohols are usually lower, and the reaction heat is less, which enables a simple adiabatic arrangement of the reactor.

Schwoegler and Adkins[1] have published the results of the amination of alcohols with ammonia and amines in the presence of a hydrogenation catalyst. From the function of the metal catalyst and from the fact that tertiary alcohols do not react under the conditions of the hydrogenation amination the authors concluded that carbonyl compounds intervene as the amination intermediates.

$$R{-}CH_2CH_2OH \rightleftarrows RCH_2CH{=}O + H_2 \qquad (A)$$

$$RCH_2CH{=}O + R'NH_2 \rightleftarrows RCH_2CH\begin{matrix} OH \\ NHR' \end{matrix} \qquad (B)$$

$$RCH_2CH\begin{matrix} OH \\ NHR' \end{matrix} + H_2 \rightleftarrows RCH_2CH_2NHR' + H_2O \qquad (C)$$

By analogy with the then accepted chemism of hydrogenation of nitriles[2] they concluded that the secondary amines are formed also by the addition of amine to imine.

$$RCH_2NH_2 \rightleftarrows RCH{=}NH + H_2 \qquad (D)$$

$$RCH{=}NH + RCH_2NH_2 \rightleftarrows RCH\begin{matrix} NH_2 \\ NHCH_2R \end{matrix} \qquad (E)$$

$$RCH\begin{matrix} NH_2 \\ NHCH_2R \end{matrix} + H_2 \rightleftarrows RCH_2NHCH_2R + NH_3 \qquad (F)$$

Rice & Kohn[3] prepared N-alkylanilines by heating aniline with alcohols to boiling in the presence of the Raney nickel catalyst. The primary alcohols with 2–6 carbon atoms gave the corresponding N-alkylanilines, the reactivity of branched-chain alcohols being much lower than that of the straight-chain alcohols. The authors produced evidence in support of the dehydrogenation step in the reaction of aniline with ethanol: when boiling ethanol with the Raney nickel they introduced the acetaldehyde formed into a solution of 2,4-dinitrophenylhydrazine to obtain the characteristic hydrazone. In a similar experiment with a mixture of aniline and ethanol the hydrazone was not formed until after the aniline has reacted. However, such evidence in support of the aldehyde as an intermediate is not unambiguous, nevertheless by 1956 the carbonyl principle of the chemism of hydrogenation amination was generally accepted.

The mechanism of hydrogenation amination of alcohols was intensively studied

in the U.S.S.R. in connection with the so-called Bashkirov process of oxidation of paraffins with air to higher alcohols. Bashkirov[4] also suggested the production of amines from alcohols using a ferric catalyst. The amination of various alcohols on the ferric catalyst was studied in the gas phase at a pressure of about 5 MPa, temperature of 200 – 270°C, and molar ratio of alcohol : ammonia : hydrogen = 1 :(10 to 50): : (6 to 50). Kliger[5,6] studied the amination kinetics on a model reaction of 1-octanol with ammonia at the temperature of 230 – 270°C. When examining the effect of the partial pressures of the reactants on the amination rate he found that the partial pressure of ammonia within the limits from 0·65 to 2·0 MPa has no effect, and the pressure of hydrogen does not affect the amination rate either. He found an extremum in the dependence of the reaction rate on the partial pressure of alcohol in the region about 200 kPa. He found a strong kinetic isotope effect in the amination of the α,α-dideuteriated 1-octanol. From these results he concluded that the rate-limiting step of the amination is the dehydrogenation of alcohol at two equivalent active centres, the other steps being fast and effectively irreversible.

Bashkirov[7] compared the kinetic isotope effect and the isotope exchange in the dehydrogenation and amination of ethanol. α-Deuteriated ethanol exhibits a strong kinetic effect in both the amination and the dehydrogenation. The isotope exchange in the alcohol is very slow in the presence of ammonia but very fast without ammonia. From the experimental results the author concluded that the splitting off of the α-hydrogen atom during the dehydrogenation of alcohol represents the rate-limiting step of the hydrogenation amination. The same conclusions were also arrived at by Fridman[8] in his analysis of the dehydrogenation of alcohols.

Baiker and Richarz[9,10] dealt with the amination of higher aliphatic alcohols in the presence of copper catalysts and found that the catalyst is rapidly deactivated in the absence of hydrogen because of the formation of surface nitride. In another paper Baiker, Caprez and Holstein[11] studied the kinetics of the reaction of 1-octanol and 1-decanol with dimethylamine and methylamine in gas and liquid phases in the presence of a copper catalyst. The energies of activation of the reaction of octanol with dimethylamine and methylamine are identical within the limits of experimental error, which confirms identical rate-limiting steps, i.e. the dehydrogenation of alcohol. The authors conclude that the dehydrogenation of alcohol and the hydrogenation of enamine (imine) are kinetically controlled, whereas the reaction of dimethylamine with aldehyde is fast and is practically thermodynamically controlled. They presume a "generally valid" mechanism of the hydrogenation amination in which the formation of amine in the hydrogenation amination of alcohol need not be connected with the imine or enamine as an intermediate, and similarly the carbonyl compound need not be an intermediate either. The carbonyl compound occurs in a "half-hydrogenated state" (RCH_2CHZOH) and reacts with the amine ($ZN(CH_3)_2$). The condensation product is the enamine in the "half-hydrogenated state" ($RCH_2CHZN.$ $.(CH_3)_2$) which is hydrogenated in the last reaction step.

In our laboratory the kinetics of the hydrogenation amination of acetone with 4-aminodiphenylamine on a copper catalyst including of the rate of formation and hydrogenation of ketimine was studied[12,13]. The formation of ketimine is not in equilibrium and, together with the hydrogenation of ketimine, affects the rate of hydrogenation amination. The reaction of amine with ketone can be accelerated by acid-base catalysts, e.g. an addition of aluminosilicate to the copper catalyst has a significant effect on the rate of the hydrogenation amination[14,15].

The model reaction of aniline with 2-propanol has been chosen for the present kinetic study of the hydrogenation amination of alcohols in the liquid phase. As well as the kinetic study of the model reaction as a whole, the individual steps were also investigated. The equilibrium constant of dehydrogenation of 2-propanol was determined, and the contribution of the catalytic reaction and of that in the homogeneous phase to the overall reaction rate has been estimated for the condensation of aniline with acetone.

EXPERIMENTAL

Reagents

Acetone p.a. (Lachema Brno); aniline (MCHZ Ostrava) was rectified before use; N-isopropylaniline (Department of Organic Technology, Prague Institute of Chemical Technology) was rectified before use; 2-propanol anhydrous p.a. (Lachema Brno) was rectified before use; electrolytic hydrogen (Technoplyn Prague); the copper(II)–chromium(III) catalyst N-203 (NIKKI Japan), 45% CuO, 45% Cr_2O_3, 5% MnO_2; the aluminosilicate WK-7122 (Leuna-Werke, G.D.R.), 80% Al_2O_3, 20% SiO_2.

Apparatus and Procedure

The experiments were carried out in a Rotamag autoclave (Development workshops, Slovak Institute of Technology, Bratislava) with the vessel of 250 ml volume of stainless steel 17246. The autoclave was equipped with three needle valves, a four-blade screw stirrer with magnetic transfer of turning moment (3 000 min^{-1}), and a thermocouple probe. The temperature course was registered by means of a TZ-21S recorder. The autoclave was heated by means of two removable electric heaters. The valve for taking samples which was placed at the bottom of the vessel was equipped with an improvised water cooler so that the volatile portions of the reaction mixture might also be condensed.

The autoclave was charged with the reaction mixture and a weighted amount of the catalyst, closed, and its free volume was washed out three times with hydrogen (each time the pressure was allowed to reach 5 MPa and released down to atmospheric pressure). After this operation, the hydrogen pressure was adjusted to 0·5 MPa and with continuous stirring the autoclave was heated to the required temperature within 6—8 min. The beginning of the reaction time was estimated by extrapolation of the conversion curve to the zero conversion. When the required temperature was reached the pressure in the system was adjusted with hydrogen. Throughout the experiment samples of the reaction mixture were taken and immediately analyzed.

The partial pressure of hydrogen was estimated as the difference between the overall pressure and the vapour tension of the reaction mixture determined experimentally.

The experimental data were evaluated by means of a HP 9835 A computer. The temperature dependences of the studied quantities were correlated by means of the program for linear regression on the function type $\ln C = A + B/T$ using the least squares criterion.

The parameters of the rate equations were calculated by the INTDAT program using the method of linear regression for estimating the parameters of the model formed by a system of differential equations linear with respect to the parameters on the basis of integral kinetic data[16,17]; moreover we used a program for integration of the kinetic model by the Merson modification of the Runge–Kutta method (RKM). The orders with respect to the individual components were determined by the method of shooting. The values of rate coefficients were calculated for the orders assessed by the INTDAT program. Using these values of parameters we carried out the integration of the kinetic model by the RKM program and, at the same time calculated the value of the criterion of the optimum estimation — the sum of squares of relative errors of concentrations of N-isopropylaniline and N-isopropylideneaniline. The calculation was continued with a new estimate of the orders with respect to the individual components.

Analytical Methods

The samples of the reaction mixture were analyzed by GLC using a CHROM 41 and a CHROM 5 apparatus (Laboratorní přístroje Prague).

The content of acetone in 2-propanol was determined by separation in a glass packed column of 1·2 m length and 3 mm inner diameter with 10% Carbowax 20 M on Chromaton N-AW-HMDS or 5% Carbowax 20 M on Inerton Super at 60°C.

The same column was used for determination of aniline, N-isopropylaniline, and N-isopropylideneaniline at 160°C.

RESULTS AND DISCUSSION

Dehydrogenation of 2-Propanol

From the course of the amination of 2-propanol with aniline (see Fig. 1) it follows that the acetone concentration in the reaction mixture is constant and, hence, thermodynamically controlled. Therefore, we studied the position of the equilibrium of dehydrogenation of 2-propanol at the reaction conditions.

The liquid-phase dehydrogenation of 2-propanol was investigated in the temperature range from 170 to 200°C and the hydrogen pressure from 1 to 3 MPa.

The equilibrium constant was calculated from the relation

$$K = c_{\mathrm{AC,eq}} c_{\mathrm{H,eq}} / c_{\mathrm{POL,eq}} \,. \tag{1}$$

Presuming that the value of Henry's constant and the density of the reaction mixture do not significantly change with composition of the reaction mixture, we can replace the equilibrium concentration of hydrogen

$$c_{\mathrm{H,eq}} = P_{\mathrm{H,eq}} / H_{\mathrm{c}} \,. \tag{2}$$

This presumption is supported by the low equilibrium concentration of acetone. For simplification, Henry's constant can be included in the equilibrium constant

$$K_D = KH_c = \frac{c_{AC,eq}P_{H,eq}}{c_{POL,eq}} = \frac{X_{AC,eq}P_{H,eq}}{1 - X_{AC,eq}}. \quad (3)$$

Table I shows the experimental data obtained for the equilibrium of the dehydrogenation of 2-propanol and the calculated values of the equilibrium constant. The temperature dependence of the experimental values of the equilibrium constant was correlated by means of the relation

$$\ln K_D = 13{\cdot}336 - 7\,555/T. \quad (4)$$

Along with the experiments studying the equilibrium of dehydrogenation of 2-propanol, an attempt was made at measuring the dehydrogenation rate. At the temperature of 180°C, pressure of hydrogen 2·4 MPa, and with 0·1 g catalyst N-203 in 150 ml of 2-propanol, the first sample of the reaction mixture taken after 15 min from the beginning of heating of the autoclave already exhibited the equilibrium content of acetone. A retardation of the dehydrogenation rate by decreasing the amount of catalyst or the temperature would not be suitable, since the catalyst amount used in the experiments of amination of 2-propanol with aniline was of a higher order

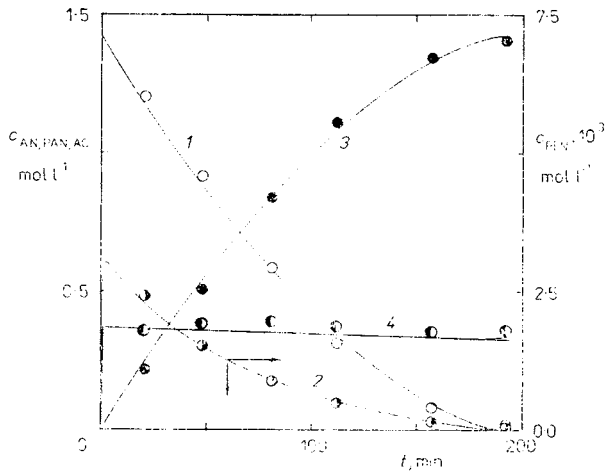

FIG. 1

The experimental and calculated time dependences of alkylation of aniline with 2-propanol. $T = 200°C$, $P_H = 2{\cdot}13$ MPa, 2 g catalyst N-203, 180 ml mixture of aniline and 2-propanol (1 : 8). *1* aniline, *2* N-isopropylideneaniline, *3* N-isopropylaniline, *4* acetone

of magnitude, and also the temperature of 180°C lies at the lower limit of the values used for amination reactions.

Condensation of Aniline with Acetone

The condensation of ketones with amines takes place even without catalysts, however, it is accelerated by acid catalysts. We tried to find the extent to which the copper–chromium catalyst participates in the condensation. At the same time we paid attention to the equilibrium of the condensation reaction.

The non-catalyzed condensation could be studied in a solution of 2-propanol, i.e. under conditions near to that of the hydrogenation amination. Therefore, these experiments were used to calculate the equilibrium constant of the condensation of aniline with acetone. When studying the effect of the catalyst, we had to use a solution of aniline in acetone only, since the catalyst would enable dehydrogenation of the alcohol and hydrogenation of ketimine.

The reaction mixture used in the experiments designed for investigating the condensation equilibrium of aniline with acetone at the temperatures 180, 190, and 200°C contained aniline and acetone of equal concentrations 2·537 mol l^{-1} (2-propanol as the solvent).

The values of rate and equilibrium constants for each temperature were determined from the rate equation

$$r_K = k_K \left(c_{AN} c_{AC} - \frac{1}{K_K} c_{PEN} c_W \right). \tag{5}$$

TABLE I

The experimental equilibrium data for the liquid-phase dehydrogenation of 2-propanol

Temperature, °C	$P_{H,eq}$, MPa	$X_{AC,eq}$	$K_D \cdot 10^2$, MPa
200	1·91	0·0361	7·153
200	1·66	0·0409	7·079
200	1·31	0·0503	6·938
200	1·08	0·0663	7·669
200	1·06	0·0645	7·308
185	1·20	0·0340	4·224
185	2·05	0·0198	4·141
170	2·92	0·0081	2·376
170	1·47	0·0168	2·512
170	1·44	0·0169	2·475

The experimental and the correlated time dependences of the concentration of N--isopropylideneaniline in the condensation of aniline with acetone are given in Fig. 2, the calculated values of the rate and equilibrium constants are presented in Table II.

The temperature dependence of the equilibrium constant of the condensation of aniline with acetone reads as follows

$$\ln K_K = -5{\cdot}57 + 926/T. \qquad (6)$$

For mathematical modelling of the amination of 2-propanol with aniline one needs to know how significant is the reaction in the volume phase compared with the catalyzed condensation of aniline with acetone. Therefore, experiments were carried out on the condensation of aniline with acetone in the absence of the catalyst and in the presence of two different concentrations of the catalyst N-203 at 180°C and with the equal initial concentrations of aniline and acetone 6·14 mol l^{-1}. The values of the rate and equilibrium constants of the condensation were calculated from Eq. (5).

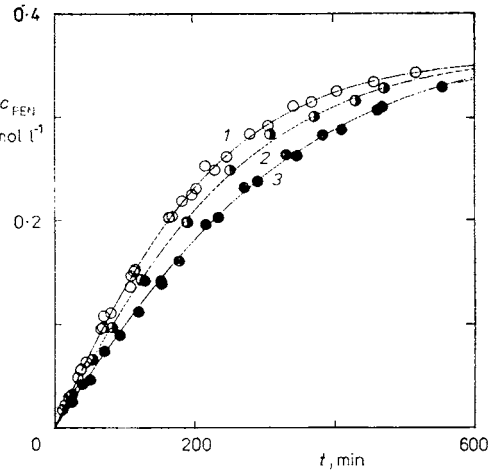

FIG. 2

The experimental and correlated time dependences of the concentration of N-isopropylideneaniline in the condensation of aniline with acetone. *1* 200°C, *2* 190°C, *3* 180°C

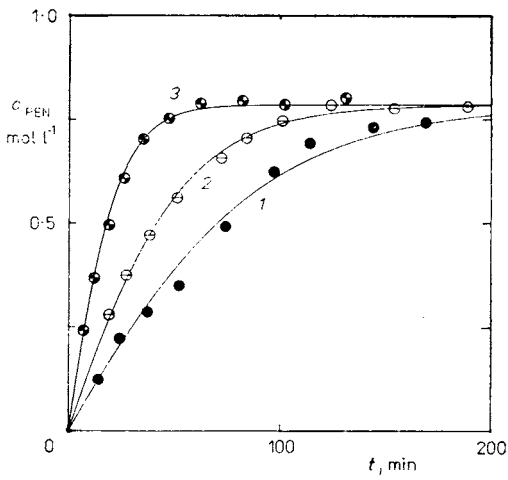

FIG. 3

The experimental and correlated time dependences of the concentration of N-isopropylideneaniline in the condensation of aniline with acetone. $T = 180$°C, concentrations of aniline and acetone 6·14 mol l^{-1}, *1* without catalyst, *2* 0·1 g catalyst N-203, *3* 0·4 g catalyst N-203

The experimental and the calculated time dependences of the N-isopropylideneaniline content are given in Fig. 3. The calculated values of the rate and equilibrium constants are presented in Table III.

The values of the rate coefficients k_K were calculated formally in the same way as those for a homogeneous reaction. The value of rate coefficient related to the catalyst can be obtained from the relation

$$k_{K,cat} = (k_K - k_K^0)/m_{cat}\,, \tag{7}$$

where k_K^0 means the rate coefficient of the non-catalyzed condensation.

Comparison of the rate coefficients k_K clearly shows that at the catalyst amount of 0·4 g per 1 mol aniline the non-catalyzed reaction represents only one quarter of the formation of N-isopropylideneaniline. In the experiments on the amination of 2-propanol with aniline, the catalyst was applied in the amounts of 8 to 20 g per 1 mol aniline, hence the amount of N-isopropylideneaniline formed by the non-catalyzed condensation is insignificant.

TABLE II

The rate and equilibrium constants for the condensation of aniline with acetone without catalyst

Temperature, °C	$k_K \cdot 10^6$, l mol^{-1} s^{-1}	$K_K \cdot 10^2$
180	2·72	2·95
190	3·32	2·78
200	3·83	2·71

TABLE III

The rate and equilibrium constants for the condensation of aniline with acetone in the presence of catalyst N-203 in 151·3 g of the reaction mixture at 180°C

Catalyst amount g	$k_K \cdot 10^6$ l mol^{-1} s^{-1}	$k_{K,cat} \cdot 10^5$ l g$_{cat}^{-1}$ mol^{-1} s^{-1}	$K_K \cdot 10^2$
0	3·98	—	2·15
0·1	6·75	2·77	2·15
0·4	15·7	2·93	2·15

Liquid-Phase Amination of 2-Propanol with Aniline in the Presence of N-203 *Catalyst*

The aim of this part of our work was to determine the relative rates of the individual reaction steps and construct, using the knowledge gained in the preceding paragraphs, a mathematical model for the alkylation of aniline with 2-propanol in the liquid phase.

The experiments were carried out at 180 and 200°C, hydrogen pressure of 2·15 and 3·15 MPa, molar ratio of aniline to 2-propanol 1 : 8 in the mixture.

The time dependences of the alkylations are given in Tables IV through VII. At the same time we followed the dependences of the parameters

$$M = c_{\mathrm{PEN},t} c_{\mathrm{W},t} / (c_{\mathrm{AC},t} c_{\mathrm{AN},t}) \tag{8}$$

$$N = c_{\mathrm{PAN},t} / (c_{\mathrm{PEN},t} P_{\mathrm{H},t}) \tag{9}$$

which provide information on how far the condensation of aniline with acetone (M) and the hydrogenation of N-isopropylideneaniline (N) are from the equilibrium. The experimentally found acetone concentrations agree well with the values calculated using the experimentally found value of the equilibrium constant. The subsequent steps are not at equilibrium, since the values of the parameters M and N do not attain constant values. In the case of the hydrogenation of N-isopropylideneaniline, the value of the N parameter increases very distinctly with the conversion of aniline, which allows the presumption that the hydrogenation of N-isopropylideneaniline is effectively irreversible.

From these findings it is possible to construct a mathematical model of the alkylation of aniline with 2-propanol:

1. The concentration of acetone can be calculated from the relation

$$c_{\mathrm{AC,eq}} = K_{\mathrm{D}} c_{\mathrm{POL,eq}} / P_{\mathrm{H,eq}} \,. \tag{10}$$

2. The rate of formation of N-isopropylideneaniline by the condensation of aniline with acetone can be expressed by the rate equation containing a correction term for the equilibrium

$$r_{\mathrm{PEN}} = k_2 c_{\mathrm{AN}}^a c_{\mathrm{AC}}^b \left(1 - \frac{c_{\mathrm{PEN}} c_{\mathrm{W}}}{c_{\mathrm{AC}} c_{\mathrm{AN}}} \frac{1}{K_{\mathrm{K}}}\right), \tag{11}$$

where K_{K} is calculated from Eq. (*6*).

The use of a rate equation with a correction term for the equilibrium is not necessary in this particular case because of the small effect of the equilibrium on the con-

TABLE IV

The amination of 2-propanol with aniline. $T = 200°C$, $P_H = 2·13$ MPa, 2 g catalyst N-203, 180 ml aniline–2-propanol mixture (1 : 8), calculated acetone concentration $c_{AC,0} = 0·37$ mol . . l^{-1}, concentrations in mol l^{-1}; $\sigma(c_{PEN}) = 6·7 . 10^{-5}$, $\sigma(c_{PAN}) = 2·7 . 10^{-2}$

t, min	c_{AC}	$c_{PEN} . 10^4$	c_{PAN}	$M . 10^3$	N, MPa^{-1}
21	0·364	24·2	0·219	1·22	42
48	0·393	15·2	0·507	2·15	156
81	0·395	8·85	0·839	3·21	444
112	0·382	4·90	1·11	4·53	1 060
157	0·360	1·48	1·34	6·83	4 260
192	0·367	0·427	1·41	9·11	15 400

TABLE V

The amination of 2-propanol with aniline. $T = 200°C$, $P_H = 3·13$ MPa, 3 g catalyst N-203, 180 ml aniline–2-propanol mixture (1 : 8), calculated acetone concentration $c_{AC,0} = 0·253$ mol . . l^{-1}, concentrations in mol l^{-1}; $\sigma(c_{PEN}) = 6·3 . 10^{-5}$, $\sigma(c_{PAN}) = 2·3 . 10^{-2}$

t, min	c_{AC}	$c_{PEN} . 10^4$	c_{PAN}	$M . 10^3$	N, MPa^{-1}
11	0·276	9·59	0·148	0·405	49
32	0·269	8·52	0·401	1·24	150
53	0·261	5·10	0·649	1·63	406
76	0·247	4·13	0·896	2·84	692
107	0·223	2·02	1·15	3·86	1 820
136	0·242	0·861	1·31	4·25	4 880

TABLE VI

The amination of 2-propanol with aniline. $T = 180°C$, $P_H = 3·2$ MPa, 5·5 g catalyst N-203, 180 ml aniline–2-propanol mixture (1 : 8), calculated acetone concentration $c_{AC,0} = 0·126$ mol . . l^{-1}, concentrations in mol l^{-1}; $\sigma(c_{PEN}) = 3·06 . 10^{-5}$, $\sigma(c_{PAN}) = 2·29 . 10^{-2}$

t, min	c_{AC}	$c_{PEN} . 10^4$	c_{PAN}	$M . 10^3$	N, MPa^{-1}
23	0·124	3·38	0·144	0·309	133
49	0·116	2·82	0·345	0·777	382
85	0·115	1·80	0·561	1·02	976
132	0·120	0·945	0·881	1·27	2 910
164	0·118	0·755	1·02	1·62	4 220

densation. However, the concentration of ketimine could approach the equilibrium concentration using a catalyst having distinctly acidic properties.

3. The rate of formation of N-isopropylaniline by the hydrogenation of N-isopropylideneaniline – with regard to the effective irreversibility – can be expressed by the relation

$$r_{PAN} = k_3 c_{PEN}^c P_H^d \,. \tag{12}$$

The system of balanced equations for N-isopropylideneaniline and N-isopropylaniline was treated by means of the HP 9 835 A computer. The experimental results from the alkylation of aniline with 2-propanol were best described by the model

$$r_{PEN} = k_2 c_{AN}^{0.3} c_{AC} \left(1 - \frac{c_{PEN} c_W}{c_{AC} c_{AN}} \frac{1}{K_K}\right) \tag{13}$$

$$r_{PAN} = k_3 c_{PEN}^{0.4} P_H^0 \,. \tag{14}$$

Table VIII presents the rate coefficients k_2 of the condensation and k_3 of the hydrogenation.

The evaluated reaction orders with respect to aniline and N-isopropylideneaniline are low which allows one to suppose that the bond between these compounds and the catalyst surface is strong. An unusual value – zero – was found for the reaction order with respect to hydrogen in the hydrogenation of N-isopropylideneaniline, and it might be explained by a strong sorption of hydrogen at the catalyst surface. The hydrogenation step is independent of the hydrogen pressure, which is an interesting phenomenon and should be looked at in later investigations (particularly by extending the range of the partial pressure of hydrogen).

TABLE VII

The amination of 2-propanol with aniline. $T = 180°C$, $P_H = 2{\cdot}2$ MPa, 5 g catalyst N-203, 180 ml aniline–2-propanol mixture (1 : 8), calculated acetone concentration $c_{AC,0} = 0{\cdot}180$ mol . . l^{-1}, concentrations in mol l^{-1}; $\sigma(c_{PEN}) = 8{\cdot}2 \,.\, 10^{-5}$, $\sigma(c_{PAN}) = 4{\cdot}2 \,.\, 10^{-2}$

t, min	c_{AC}	$c_{PEN} \,.\, 10^4$	c_{PAN}	$M \,.\, 10^3$	N, MPa^{-1}
14	0·169	5·90	0·114	0·304	88
49	0·168	5·07	0·400	1·18	358
83	0·180	3·41	0·680	1·73	907
114	0·174	2·45	0·951	2·84	1 760
151	0·154	1·15	1·21	4·13	4 780
183	0·165	0·99	1·34	9·70	6 160

Amination of 2-Propanol with Aniline on N-203 *Catalyst with Addition of Aluminosilicate*

The condensation of ketones with amines is catalyzed by acids, hence an addition of aluminosilicate should accelerate the amination. Table IX gives the time dependences of two amination experiments with different concentrations of aluminosilicate. The addition of 0·5 g aluminoslilicate to 2 g copper–chromium catalyst

TABLE VIII

The rate constants k_2 for the condensation of aniline with acetone and k_3 for the hydrogenation of N-isopropylideneaniline evaluated from the mathematical model of the alkylation of aniline with 2-propanol

T °C	$k_2 \cdot 10^5$ $l^{1.3}\,mol^{-0.3}\,s^{-1}\,g_{cat}^{-1}$	$k_3 \cdot 10^4$ $l^{0.4}\,mol^{0.6}\,s^{-1}\,g_{cat}^{-1}$
180	2·99	1·00
200	4·68	1·94

TABLE IX

The amination of 2-propanol with aniline with addition of aluminosilicate. $T = 200°C$, $P_H = 2·13$ MPa, 2 g catalyst N-203, 180 ml aniline–2-propanol mixture (1 : 8), concentrations are expressed in mol l^{-1}

t, min	c_{AC}	$c_{PEN} \cdot 10^3$	c_{PAN}	$M \cdot 10^3$
		0·5 g aluminosilicate		
14	0·382	3·96	0·560	6·79
29	0·392	1·79	0·850	6·79
44	0·373	1·27	1·03	8·92
59	0·373	0·846	1·16	9·97
79	0·395	0·755	1·28	16·97
		0·25 g aluminosilicate		
12	0·370	3·92	0·371	3·78
37	0·374	1·48	0·752	4·44
61	0·394	0·855	0·993	5·00
86	0·373	0·584	1·14	6·28
115	0·365	0·470	1·25	9·23
146	0·384	0·356	1·32	11·7

increased the rate of formation of N-isopropylaniline considerably. The comparison of the values of the M parameter with the experiment without aluminosilicate (Table IV) shows that aluminosilicate shifts the concentration of ketimine nearer to the equilibrium.

CONCLUSION

It was proved that in the reaction of aniline with 2-propanol on the copper(II)–chromium(III) catalyst the formation of acetone is thermodynamically controlled. In the batch experiments with excess 2-propanol, the acetone concentration is constant in the reaction mixture and corresponds to the experimentally found equilibrium. This contradicts the statement by Baiker[11] saying that the dehydrogenation of alcohols is rate-limiting in the aminations of both primary and secondary alcohols. Obviously, the authors mechanically extrapolated the results obtained for the aminations of primary alcohols to secondary alcohols. The overall rate of amination of 2-propanol with aniline is determined by the condensation of acetone with aniline and co-determined by the hydrogenation of ketimine. The acceleration of the amination observed after addition of aluminosilicate to the copper(II)–chromium(III) catalyst confirms that the concentration of ketimine in the reaction mixture is not thermodynamically controlled.

SYMBOLS

AC	acetone
AN	aniline
c	molar concentration
H	hydrogen
H_c	Henry's constant
K	equilibrium constant
k	rate coefficient
m	mass
M	parameter for the condensation of aniline with acetone
N	parameter for the hydrogenation of imine
P	pressure
PAN	N-isopropylaniline
PEN	N-isopropylideneaniline
POL	2-propanol
r	reaction rate
T	temperature
t	time
W	water
X	conversion
Z	active center
σ	standard deviation

Indexes

D	dehydrogenation
eq	equilibrium state
K	condensation
cat	catalyst
0	initial value
t	the value at the time t

REFERENCES

1. Schwoegler E. J., Adkins H.: J. Am. Chem. Soc. *61*, 3499 (1939).
2. Braun J., Blessing G., Zobel F.: Chem. Ber. *36*, 1988 (1923).
3. Rice R. G., Kohn E. J.: J. Am. Chem. Soc. *77*, 4052 (1956).
4. Bashkirov A. N., Kagan Yu. B., Kliger G. A.: U.S.S.R. 133 889 (1960).
5. Kliger G. A., Bashkirov A. N., Schneider P., Rozovskii A. Ya., Lesik O. A., Markhevskaya E. V., Kagan Yu. B.: Neftekhim. *8*, 283 (1968).
6. Kliger G. A., Lazutina L. F., Fridman R. A., Kryukov Yu. B., Bashkirov A. N., Snagovski Yu. S., Smirnova R. M.: Kinet. Katal. *16*, 660 (1975).
7. Bashkirov A. N., Fridman R. A., Bogolepova E. I., Smirnova R. M., Kryukov Yu. B.: Dokl. Akad. Nauk SSSR *201*, 847 (1971).
8. Fridman R. A., Bogolepova E. I., Kryukov Yu. B., Bashkirov A. N.: Neftekhim. *15*, 426 (1975).
9. Baiker A., Richarz W.: Ind. Eng. Chem., Prod. Res. Dev. *16*, 261 (1977).
10. Baiker A.: Ind. Eng. Chem., Prod. Res. Dev. *20*, 615 (1981).
11. Baiker A., Caprez W., Holstein W. L.: Ind. Eng. Chem., Prod. Res. Dev. *22*, 217 (1983).
12. Pašek J.: *Thesis*. Prague Institute of Chemical Technology, 1980.
13. Pašek J., Čmok M., Pexidr V.: Chem. Prum. *38*, 73 (1988).
14. Volf J., Pašek J.: Chem. Prum. *28*, 464 (1978).
15. Volf J., Pašek J., Mašek J., Řežábek A.: CS 179 110 (1975).
16. Himmelblau D. M., Jones C. R., Bischoff K. B.: Ind. Eng. Chem., Fundam. *6*, 539 (1967).
17. Jiráček F., Hanika J.: *Technologické algoritmy*. SNTL, Prague 1978.

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