CATALYTIC HYDROGENATION OF C = N BOND

COMMUNICATION 1. STUDY OF HYDROGENATION OF AZOMETHINES OF BENZYLIDENE SERIES

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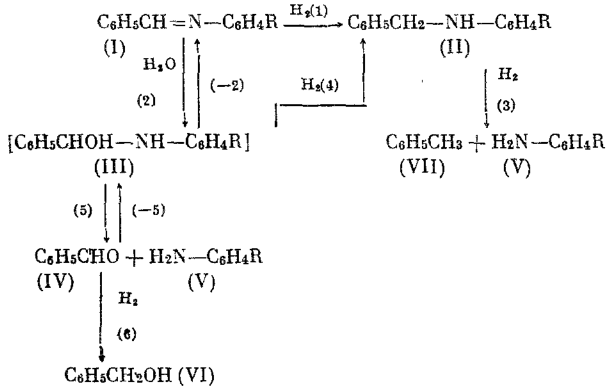
A study of the rules for the catalytic hydrogenation of the C = N bond in azomethines is of interest from the standpoint of ascertaining the relation between the reactivity of the hydrogenated compound and its structure. Only a small amount of data exists in the literature that relates to this problem. The hydrogenation of some azomethines in the presence of PtO_2 [1], $[Co(CN)_5]^{-3}$ [2], and bis(dimethylglyoximato) cobalt(II) [3] is described. In the last two cases a correlation was observed between the reaction rate and the basicity of the azomethines.

In the present paper we studied the hydrogenation of some azomethines of the benzylidene series with different substituents in the aniline portion of the molecule. The reaction was run in ethanol at atmospheric pressure and 20°C in the presence of 5% Pd/C.

As the hydrogenation objects we used azomethines of general formula $C_6H_5CH{=}N{-}C_6H_4R$, where R = H, o-, m-, p-CH_3, o-, p-OCH_3. The reactions that can proceed during the catalytic hydrogenation of azomethines are shown in the following scheme.



The change in the composition of the reaction mixture during the hydrogenation of (I) (R=H, o-, m-, p-CH_3, o-, p-OCH_3) is given in Table 1. The curves for the change in the composition of the mixture (I, R = H) are plotted in Fig. 1; the curves for the o-, m-, and p-methyl-substituted azomethines have a similar shape. From Table 1 and Fig. 1 it can be seen that the hydrogenation of the C = N bond proceeds selectively under the studied conditions. In the initial moments of reaction the main component of the mixture is the azomethine (I), the amount of which decreases and reaches zero toward the end of absorbing 1 mole of H_2. The predominant component becomes the secondary amine (II). Its amount reaches a maximum at the point of absorbing the first mole of H_2, which corresponds to the formation of (II) via the hydrogenation of the C = N bond [reaction (1)]. Then the amount of (II) drops to zero due to hydrogenolysis of the secondary amine [reaction (3)]. The obtained data show that equimolar amounts of amine (V) and aldehyde (IV) are formed up to the absorption of 0.5-0.6 mole of H_2. Their concentration decreases somewhat up to the point of absorbing the first mole of H_2, and then the amount of (V) increases sharply after the hydrogenoly-

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TABLE 1. Hydrogenation of Azomethines $C_6H_5CH=N-C_6H_4R$ [1.5 mmoles of (I), 0.15 g of 5% Pd/C, 15 ml of absolute ethanol, 20°]

R in starting azomethine	Hydrogenation rate · 10^4, mole/min · g of cat.	H_2 absorption, moles	Reaction products, mole %				
			azomethine (I)	secondary amine (II)	aldehyde (IV)	amine (V)	toluene* (VII)
H	5,2±0,5	0,13	77,5	9,9	5,9	7	—
		0,35	63,5	25	5,8	5,72	—
		0,51	39,5	45	7,35	7,9	—
		0,59	34,9	54	4,95	6,6	—
		0,92	—	83	3,2	8,8	5,6
		0,94	—	77	3,4	11,6	8,2
		1,48	—	34,5	1,9	32	30,1
o-CH_3	4,7±0,4†	0,28	64,2	32,2	—	3,6	—
		0,59	34	65	—	—	—
		0,96	—	95,5	—	4,64	—
		1,3	—	38	—	31	31
		1,73	—	—	—	50	50
		1,94	—	—	—	50	50
m-CH_3	3,7±0,2	0,2	52	24	12,8	13,2	—
		0,5	30,6	43	12	13,8	—
		0,85	7,2	64	9	14,8	5,8
		1	5,5	62	7,2	17	9,8
		1,63	—	23,5	3,85	36	32,2
p-CH_3	3,8±0,4	0,1	70,5	2,85‡	13,8	13	—
		0,32	55	19,5	13,3	13,3	—
		0,61	34	45,5	9,3	11	—
		0,97	5,2	70,5	5,5	12,2	6,7
		1,08	—	69	4,5	16	11,5
		1,71	—	9,8	2,8	45,5	42,7
o-OCH_3	7,2±0,3†	0—1			Traces		—
p-OCH_3	4,0±0,1	0—1			Is present	Is present	—

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* The calculation is based on the excess amount of amine (V) relative to aldehyde (IV), which shows the extent of hydrogenolysis of (II).

† Taking the threshold catalyst concentration into account.

‡ Calculated from the amount of absorbed H_2.

sis of (II) starts. This indicates that hydrolysis of the C=N bond occurs in the initial moments of reaction. The presence of hydrolysis products in the reaction mixture indicates that the C=N bond is very sensitive to water. It should be mentioned that the reaction was run in absolute alcohol, but the conditions of preparing the experiment did not exclude contact of the substrate and solvent with atmospheric moisture. Calculation shows that even 0.25% of water in the alcohol is sufficient to completely hydrolyze the 1.5 mmoles of (I) taken for reaction. If judged by the amount of aldehyde (IV), then the degree of hydrolysis is 7-13 mole %. A comparison of the relative amounts of hydrolysis products in the catalyzates with the control alcohol solutions of (I) shows that the hydrolysis is accelerated by the catalyst [reactions (2) and (5)]. This finds confirmation in the fact that the degree of hydrolysis of (I) does not correlate with the hydrolysis rate constants (k) and the reciprocal values of the formation equilibrium constants (1/K), which were determined in aqueous alcohol mixtures [4].

A comparison of the character of the hydrogenation of various azomethines reveals that the cleanest hydrogenation occurs in the case of (I, R=o-CH_3), where hardly any hydrolysis is observed. Hydrolysis is observed for the unsubstituted azomethine and to a somewhat greater degree for the p- and m-methyl derivatives.

Since the corresponding azomethines decomposed at the temperatures needed to run the GLC analysis of the reaction mixture (I, R=o-, p-OCH_3), we were unable to obtain quantitative data on the initial hydrolysis. Analysis of the reaction mixture (I, R=o-OCH_3) at a lower temperature (150°) reveals the presence of only traces of (IV) and (V), which suggests a very slight degree of hydrolysis. The chromatograms (I, R=p-OCH_3) show the presence of (IV) and (V), which testifies that hydrolysis occurs in the initial stages of the reaction. The absence of toluene (VII) in the samples up to the absorption of 1 mole of H_2 testifies to the fact that also in (I, R=o-, p-OCH_3) the hydrogenolysis of the benzyl–N bond begins only after the absorption of the first mole of H_2.

From Table 1 it follows that up to the absorption of 0.6-0.8 mole of H_2 the hydrogenation of the C=N bond is not complicated by other processes that are associated with the consumption of H_2. Actually, the

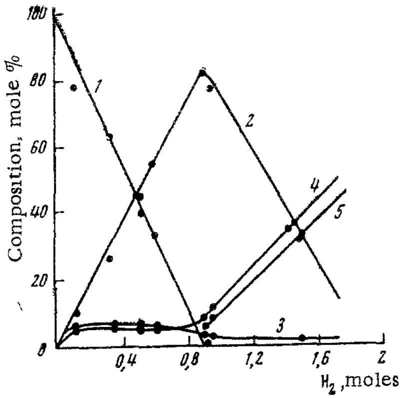

Fig. 1

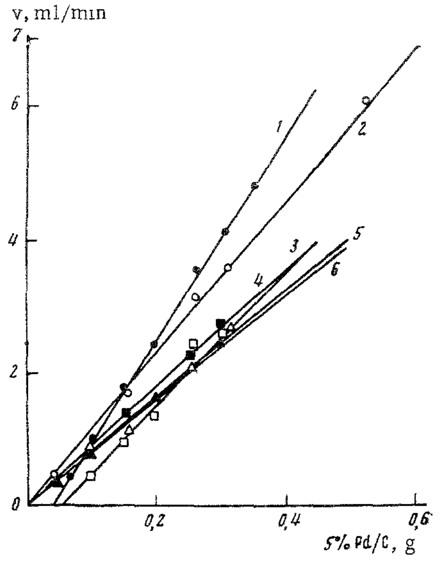

Fig. 2

Fig. 1. Composition of reaction mixture as a function of amount of absorbed H_2 [1.5 mmoles of (I), 15 ml of alcohol, 0.15 g of 5% Pd/C, 20°]: 1) $C_6H_5CH{=}N{-}C_6H_5$; 2) $C_6H_5CH_2{-}NH{-}C_6H_5$; 3) $C_6H_5{-}CHO$; 4) $C_6H_5{-}NH_2$; 5) $C_6H_5{-}CH_3$.

Fig. 2. Hydrogenation rate of azomethine (I) as a function of amount of catalyst when R is: 1) o-OCH_3; 2) H; 3) o-CH_3; 4) p-OCH_3; 5) p-CH_3; 6) m-CH_3.

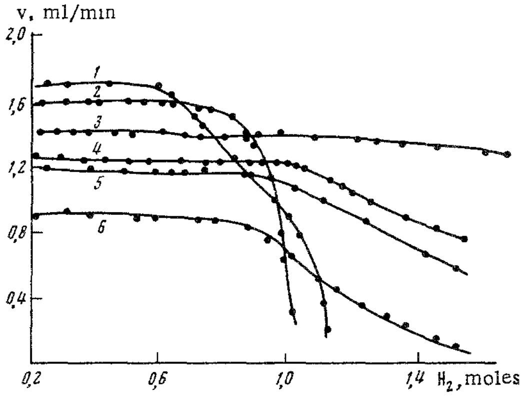

Fig. 3. Hydrogenation rate of azomethines as a function of amount of absorbed H_2 [1.5 mmoles of (I), 15 ml of alcohol, 0.15 g of 5% Pd/C, 20°] when R is: 1) o-OCH_3; 2) H; 3) p-OCH_3; 4) p-CH_3; 5) m-CH_3; 6) o-CH_3.

H_2 absorption due to the hydrogenation of benzaldehyde to benzyl alcohol [reaction (6)] in this range does not exceed 1-2%. Consequently, the rate of H_2 absorption in the range up to 0.6 mole of H_2 can be considered to be a measure of the hydrogenation rate of the $C{=}N$ bond, all the more so since the amount of (II) in the catalyzate, determined by GLC, corresponds to the degree of conversion that was calculated from the amount of absorbed H_2.

The hydrogenation rate (I, R = o-OCH_3) is independent of the initial substrate concentration in the studied concentration range of $0.79 \cdot 10^{-2}$-$2.11 \cdot 10^{-2}$ g/ml. This makes it possible to assume that the hydrogenation up to the conversion of 0.6-0.8 mole of H_2 obeys the zero order in hydrogenated compound (I). The effect of the catalyst amount on the hydrogenation rate is proportional to the amount of catalyst taken for reaction (Fig. 2). It should be mentioned that a threshold catalyst concentration (0.04-0.05 g of 5% Pd/C) was observed for the o compounds (I; R = o-CH_3, o-OCH_3).

The hydrogenation curves in the presence of 0.15 g of 5% Pd/C (Fig. 3) show that the hydrogenation goes at a constant rate in the range up to 0.6-0.8 mole of H_2, and only after this does the H_2 absorption rate decrease. This last section of the curve corresponds to hydrogenolysis. In the case of (I, R = H) the reaction becomes much slower (b ~ 50 times) after the absorption of 1 mole of H_2. For (I, R = p-OCH_2) the rates for hydrogenation of the C = N bond and hydrogenolysis of the benzyl—N bond are practically equal. At the same time, hydrogenolysis is not observed until the hydrogenation of (I) is nearly complete. This can be explained by the fact that the hydrogenolysis of (II) cannot begin as long as the catalyst surface is occupied by (I). The picture observed for the other azomethines lies intermediate between these two cases. The sequence of the hydrogenation (1) and hydrogenolysis (3) reactions is found to be in harmony with the values of the energy barriers of these reactions, respectively −23 and −31.4 kcal, which were calculated on the basis of the multiplet theory [5].

A comparison of the hydrogenation rates of various azomethines (see Table 1) reveals that the insertion of electron-donor substituents into the amino ring of (I) has very little effect on the hydrogenation rate, and causes a slight decrease in the rate in the case of the m-CH_3, p-CH_3, and p-OCH_3 groups. The presence of substituents in the o position causes some increase in the hydrogenation rate when comparied with the m and p substituents.

EXPERIMENTAL METHOD

The azomethines were obtained as described in [6], and the melting points, as well as the IR and UV spectra, coincided with the literature data. As the hydrogenation catalyst we used 5% Pd/C [7]. The hydrogenation was run in a thermostatted duck (hydrogenation vessel) at 20° in absolute ethanol. The H_2 absorbed during reaction was measured via a gas buret (0.5-ml graduations), while the catalyzate samples were analyzed by GLC. The limiting rate was reached at 600-700 turns/min. The hydrogenation experiments were performed mainly at an azomethine concentration of 10^{-4} mole/ml, and the amount of catalyst ranged from 0.05 to 0.5 g in 15 ml of solvent. The products were analyzed on LCM-5 and LCM-8MD chromatographs, using a catharometer as the detector, a helium flow rate of 40 ml/min, and a 3m × 3 mm-column (azomethines I, R = H, o-, m-, p-CH_3), and a flame-ionization detector, nitrogen flow rate of 43 ml/min, and programmed heating in the range 150-200° at a rate of 8 deg/min (azomethines I, R = o- and p-OCH_3). Compounds (I), (II), (IV), and (V) (R = H, o-, m-CH_3), were separated on a column packed with QF_1 deposited on Celite 545. The separation of (I) from (II), and (IV) from (VI), could not be achieved when R = p-CH_3. The ratios of (I) and (II) were calculated from the amount of H_2 absorbed during hydrogenation. The separation of (IV) and (VI) was accomplished on a column packed with Carbowax deposited on silanized Chromatone. The separation of (I) and (II) failed to occur in the case of (I, R-o-, p-OCH_3) and, in addition, the chromatographing of (I) was accompanied by decomposition of the compound. For this reason only a qualitative check was made. The hydrogenolysis and hydrolysis processes were judged by the presence of toluene (VII), aldehyde (IV), and amine (V) on the chromatograms that were obtained at low temperatures, where (I) and (II) remain in the column. The retention times (min) of the azomethines and their transformation products on QF_1 are as follows. R = H: (II) 17.1, (I) 14.5, (VI) 2.0, (IV) 1.95, (V) 1.7 (142°, 50 ml/min). R = o-CH_3: (II) 19.9, (I) 18.8 (V) 2.3 (147°, 43 ml/min). R = m-CH_3: (II) 22.5, (I) 21.6, (V) 2.15 (143.5° 50 ml/min). R = p-CH_3: (II) 23.6 (I) 23.2, (V) 2.15 (142°, 50 ml/min). R = o-OCH_3: (II) 9.3, (I) 9.0 (V) 2.3. R = p-OCH_3: (II) 10.2, (I) 9.6 (V) 1.6 (150-200°, 8 deg/min, 43 ml/min). On Carbowax/Chromatone: (IV) 6.8, (VI) 22.8 (159°, 42 ml/min). For (I, R = H) and its hydrogenation products the calibration was done using dodecyl alcohol as the internal standard. The correction factors for all of the compounds are close to one. Analysis of the catalyzates using an internal standard gives a total yield of the products that is close to 100%, and for this reason a quantitative analysis of the separate samples of the entire series of azomethines was done by the internal normalization method.

CONCLUSIONS

1. The hydrogenolysis of benzylideneaniline, and of its methyl and methoxy derivatives, in the presence of Pd/C proceeds selectively: the hydrogenolysis of the benzyl—N bond begins only after the absorption of the first mole of hydrogen.

2. Partial hydrolysis of the C = N double bond occurs under the hydrogenation conditions due to traces of water in the solvent.

3. The insertion of electron-donor substituents into the benzene ring, attached to the nitrogen, has little effect on the hydrogenation rate of the azomethine. The o-substituted azomethines hydrogenate somewhat faster than do the m- and p-substituted derivatives.

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