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SOME FEATURES OF THE SYNTHESIS OF URETHANES BY THE CARBONYLATION OF NITROBENZENES IN ALCOHOLIC SOLUTION

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A promising route for the synthesis of urethanes, which are used extensively in the national economy as nontoxic herbicides, is by the carbonylation of nitro compounds in alcoholic solution in the presence of Pd catalysts [1]. The use of pyridine, V_2O_5 [2], and $FeCl_3$ [3] as a activators for the Pd catalysts has been suggested. We have found that VCl_3 is a more active promoter in the system $PdCl_2$–pyridine. This communication describes the principal features of this industrially important reaction, taking as an example the carbonylation of nitrobenzenes in ethanol in the presence of the catalyst $PdCl_2$–VCl_3–pyridine. This information is not available in the literature.

EXPERIMENTAL

The reaction was carried out in an autoclave of capacity 0.15 liter, into which was charged 10 ml of an ethanolic solution containing 2 mole/liter of the nitro compound, 2 mole/liter of pyridine, and the catalyst. The autoclave was flushed out with CO, the CO pressure raised to 8 MPa, and the autoclave heated at the required temperature for 10-150 min. The reaction products were analyzed on an LKhM-8MD chromatograph (column length 1 m, with 5% XE-60 on Chromaton N-AW-DMCS, 0.2 mm, katharometer detector, He carrier gas flow rate 40 ml/min), the column temperature being programmed from 80 to 230°C at a rate of 20°/min.

DISCUSSION OF RESULTS

Over the range of reaction times from 5-150 min, nitrobenzene, 4-methylnitrobenzene, and 2-chloronitrobenzene were reduced at virtually the same rate (Fig. 1). The plots for the reaction of the nitro compounds coincide, and up to 70% conversion the linearity of the plot of conversion against reaction time is maintained. The nature of the substituent in the nitro-compound affects only the selectivity of formation of the corresponding urethane, the yields of carbamates decreasing in the sequence ethyl N-4-methylphenyl- > ethyl N-phenyl- > ethyl N-2-chlorophenylcarbamate. The yields of carbamates increased linearly up to 50-60 min, and thereafter remained unchanged. Stabilization of the yields of urethanes was observed at a conversion of the starting nitro compound of 50-70%.

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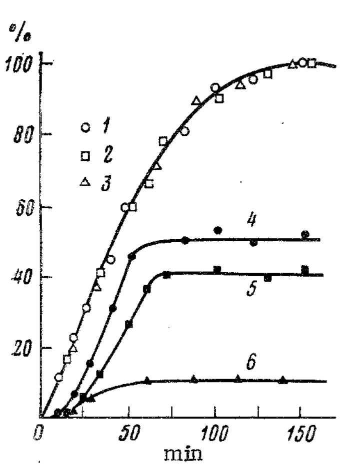


Fig. 1

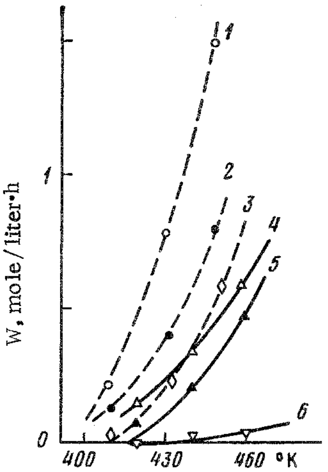


Fig. 2

Fig. 1. Influence of reaction time on the conversion of 4-methylnitrobenzene (1), nitrobenzene (3), and 2-chloronitrobenzene (5), and the yields of ethyl N-4-methylphenylcarbamate (2), ethyl N-phenylcarbamate (4), and ethyl N-2-chlorophenylcarbamate (6) at 453°K, $[PdCl_2]$ = 1 mmole/liter, $[VCl_3]$ = 12 mmole/liter.

Fig. 2. Effect of reaction temperature on the initial rate of reduction of nitrobenzene (1, 4), and the formation of ethyl N-phenylcarbamate (2, 5) and aniline (3, 6) in the presence of 12 mmole/liter of VCl_3 (1-3) and 12 mmole/liter of $FeCl_3$ (4-6), at $[PdCl_2]$ = 1 mmole/liter.

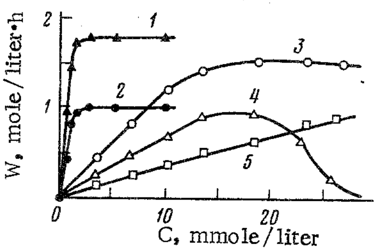
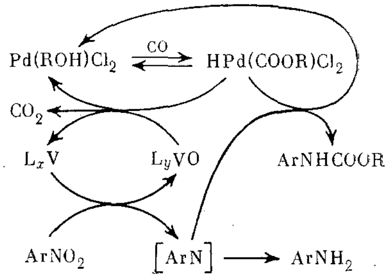


Fig. 3. Plots of the rate of reduction of nitrobenzene (1,3) and of the formation of ethyl N-phenylcarbamate (2, 4) and aniline (5) against $PdCl_2$ concentration (1, 2) and VCl_3 concentration (3, 5) in solution, when $[PtCl_2]$ = 1 mmole/liter (3-5) and $[VCl_3]$ = 12 mmole/liter (1, 2) at 453°K.

Starting from these findings, the effects of temperature and catalyst composition of the initial reaction rate of the nitro compounds in ethanol was examined, using as an example the synthesis of ethyl N-phenylcarbamate with $PdCl_2$–VCl_2 (Cat 1) and $PdCl_2$–$FeCl_3$ (Cat 2) as catalysts. The results are shown in Fig. 2. In the presence of Cat 1, as well as Cat 2, when the temperature is raised over the range 400-460°K the initial rate of reduction of nitrobenzene and formation of the carbamate and the by-product aniline aniline increase by a factor of 6-7. Palladium chloride was inactive in the absence of a promoter. The reaction likewise did not proceed with VCl_3 or $FeCl_3$ in the absence of $PdCl_2$. The activating effect of VCl_3 was 2-3 times greater than the known promoter, $FeCl_3$.

As the concentration of $PdCl_2$ was increased to 2 mmole/liter when the concentration of VCl_3 was held constant at 12 mmole/liter, or when the concentration of VCl_3 was increased to 15 mmole/liter at a concentration of $PdCl_2$ of 1 mmole/liter, the rate of reduction of nitrobenzene and the formation of carbamate and aniline increased from zero to 1.8, 1.0, and 0.6 mole/liter·h, respectively (Fig. 3). Further increase in the concentration of $PdCl_2$ or VCl_3 had no effect on the rate of reduction of nitrobenzene.

These findings lead to the conclusion that at concentrations of $PdCl_2 < 2$ mmole/liter and $VCl_3 < 15$ mmole/liter, the rate of synthesis of carbamates will be determined by the slow step of conversion of the components of the catalyst ($PdCl_2$ and VCl_3), or more precisely the compounds into which they are converted by reaction with the reactants, in accordance with the scheme



L = Cl, Py.

This scheme is based on the known property of palladium compounds to form with alcohols and CO carboxylate complexes which are intermediates in the oxidation of CO to carbonates and CO_2, as well as in the formation of carbamates [4].

CONCLUSION

1. The activating effect of VCl_3 on $PdCl_2$ has been established in the synthesis of carbamates by the carbonylation of nitrobenzenes in ethanol solution.

2. The principle features of the reaction have been established, and a generalized scheme for the reaction proposed.

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