HYDROGENATION OF SUCCINIMIDE TO PYRROLIDIN-2-ONE

I. Influence of the Solvent on the Catalytic Reduction of Succinimide

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The influence of the nature of the solvent on the hydrogenation of succinimide over Raney nickel was studied. The greatest rates of reduction of the imide and of the formation of pyrrolidinone were found when alcohols and dioxane were used. An influence of the solvent on the ratio of the rates of the various stages in the synthesis of pyrrolidinone from the imide was found.

One of the possible methods for obtaining pyrrolidinone is the reduction of succinimide. Methods for the electrochemical reduction of succinimide [1, 2] and for reduction with nascent hydrogen [3] have recently been described, but its catalytic hydrogenation has so far been studied very little. The information available in the literature on the possibility of performing this reaction is mostly from patents and relates mainly to the reduction of N-substituted succinimides [4, 5, 6] which takes place considerably more readily than that of the unsubstituted compound [6]. There is also information on the reduction of substituted succinimide and phthalimide with metal hydrates [7, 8].

In the present work we have investigated the influence of various solvents for succinimide on the rate of its reduction, and on the yield of pyrrolidinone. This study is necessary because the hydrogenation of succinimide in the absence of a solvent takes place at a negligible rate and is accompanied by the formation of large amounts of by-products. As the solvent in this reaction dioxane, tetrahydrofuran, methoxyethanol, methylcyclohexane, and water have been used previously [4, 6, 8]. Under these conditions the yield of pyrrolidinone was 50–80% of the theoretical amount, but the rate of hydrogenation was low. In a discontinuous apparatus with the catalyst in an amount of 10% of the weight of the raw material the process lasts from 3 to 10 hr. We studied the kinetics of the hydrogenation of succinimide and the formation of pyrrolidinone on Raney nickel at elevated temperatures and pressures in solvents of various classes: water, n-octane, cyclohexane, diisopropyl ether, dioxane, and normal and iso alcohols. The experiments were carried out under similar conditions: standard concentrations of imide, catalyst, and solvent, and identical temperature and pressure.

According to our results (Table 1, Figs. 1 and 2), the best media for the catalytic reduction of succinimide are alcohols and dioxane. In these solvents the rate of hydrogenation is almost an order of magnitude higher than in water, aliphatic or alicyclic hydrocarbons, or ethers. The highest rate of absorption of hydrogen is found in the primary butanols. Conversely, in tertiary butanol the rate of the reaction is the lowest among the solvents of this group.

Considerable differences in the rates of formation of pyrrolidinone (at the same rates of absorption of hydrogen)

Table 1. Influence of the Nature of the Solvent on the Hydrogenation of Succinimide over Raney Nickel at 230° C and 200 Atmospheres*

Time, min	ΣH_2					Dioxane		Methanol		Ethanol		Propan-1-ol		Butan-1-ol	
	Water	n-octane	cyclohexane	diisopropyl ether	2-methylpropan-2-ol	ΣH_2	$\Sigma \Pi$	ΣH_2	$\Sigma \Pi$	ΣH_2	$\Sigma \Pi$	ΣH_2	$\Sigma \Pi$	ΣH_2	$\Sigma \Pi$
20	4.2	0.8	2.3	0.7	12.5	36.0	22.4	40.5	8.1	49.0	26.9	41.3	28.5	46.8	30.9
40	6.5	1.8	3.6	1.4	25.2	52.8	30.8	57.5	16.3	60.8	34.3	67.5	40.8	85.8	44.6
60	9.7	4.3	5.1	2.1	37.8	66.8	39.3	72.6	21.6	76.3	45.9	81.4	44.3	100.3	48.7
80	13.6	4.5	7.0	2.6	49.5	73.8	45.7	85.8	25.8	89.0	49.9	92.7	46.7	108.1	51.3
100	16.9	6.4	7.7	3.2	54.7	85.0	59.0	98.7	26.9	92.0	46.8	103.3	49.3	114.1	53.5
120	20.6	7.3	8.4	3.7	57.8	88.7	60.8	110.0	26.0	102.0	46.6	115.1	47.0	118.0	56.8

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*ΣH_2 represents the amount of hydrogen absorbed as a percentage of the amount theoretically necessary for the reduction of the imide to pyrrolidinone. ΣP is the amount of pyrrolidinone formed as a percentage of the theoretical yield.

in the various solvents must be mentioned. This may be due to the influence of the solvent on the selectivity of reduction of succinimide to pyrrolidinone, on the rate of the further hydrogenolysis of the pyrrolidinone, and on the ratio of the rates of the various chemical stages in the formation of the lactam from the imide. While the existence of the first two factors is shown by the fact that the amount of hydrogen used in the reaction is greater than that necessary for reduction simply to the pyrrolidinone and by the presence of maxima on the curves for the change in the concentration of pyrrolidinone with time, to illustrate the last-mentioned phenomenon we compare the rates of absorption of hydrogen, of consumption of succinimide, and of formation of the pyrrolidinone in one and the same solvent. We see from Fig. 1 that the amount of hydrogen necessary to convert the succinimide into pyrrolidinone is absorbed in ~40 min from the start of the reaction, and the succinimide reacts almost completely. The first parts of the hydrogen-absorption curve and the curve for the change in the concentration of the imide coincide. The accumulation of pyrrolidinone, takes place by a different mechanism and its concentration in the hydrogenate continues to rise even after the disappearance of the succinimide, reaching its maximum at the 70-th min. The difference of 30 min between the disappearance of the succinimide and the time of maximum concentration of the pyrrolidinone shows the existence of an intermediate stage. In this solvent, the limiting stage is that of pyrrolidinone-formation.

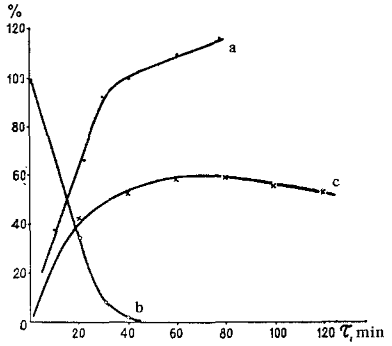

Fig. 1. Curves for (a) the absorption of hydrogen, (b) the consumption of succinimide, and (c) the accumulation of pyrrolidinone as functions of time (in 2-methylpropan-1-ol).

Precisely the same pattern was observed when normal butanol was used as the solvent. In other alcohols (with the exception of ethanol) and also in dioxane where the hydrogenation of the imide takes place somewhat more slowly than in the butanols, the existence of a limiting stage is not as marked (Fig. 2). In methanol, ethanol, and the propanols, the rates of absorption of hydrogen are almost the same, but the formation of pyrrolidinone in methanol takes place considerably more slowly and here again the existence of a limiting stage is shown. The difference in the rates of accumulation of pyrrolidinone, although the rates of absorption of hydrogen are similar in these alcohols, can be explained if we assume the possible participation of the solvent in the formation of the intermediate substance or complex.

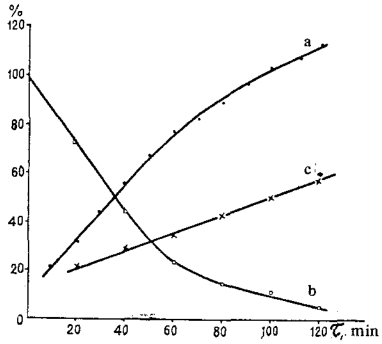

Fig. 2. Curves for (a) the absorption of hydrogen, (b) the consumption of succinimide, and (c) the accumulation of pyrrolidinone as functions of time (in propan-2-ol).

In a study of the influence of the initial concentration of succinimide on the rate of its hydrogenation in various solvents, it was found that in propan-2-ol the rate of hydrogenation begins to decrease only at a molar ratio of imide to alcohol ≥ 1 (Table 2). In dioxane, however, reduction must be carried out in a large excess of solvent, since even a small increase in the initial concentration of the dissolved substance has an adverse effect on the rate of the process (Fig. 3).

Table 2. Influence of the Initial Concentration of Succinimide in Isopropanol on the Rate of Hydrogenation

Time, min	Amount of hydrogen absorbed (%) at various initial concentrations of succinimide (mole %)					
	9,1	13,0	16,7	23,0	50,0	60,0
10	21.8	19.8	18.9	19.3	19.0	5.1
20	32.7	31.6	28.9	32,5	30.7	9.3
30	44.1	41.3	44.0	48.8	40.5	13.5
40	55.5	52,7	55,3	59.5	49.0	19.0
50	67.2	63.1	66,4	69.2	55.6	23.5
60	76.1	76.5	72,2	76.8	59.8	28.0
70	82.1	78.9	79,1	85,8	62,5	32,5
80	88.0	82.3	83,2	89,1	65,6	37,2

EXPERIMENTAL

The experiments were carried out in a 0.5-*l* autoclave having an electromagnetic drive of the Vishnevskii design [9] and fitted with a capillary sampling device. Hydrogen, freed from traces of moisture and oil, was fed into the autoclave from a graduated measuring vessel. During the experiments the pressure was maintained at 200 atm and the temperature at 230 ± 1° C. In all the experiments (except for those on the influence of the concentration of the solute) the charge was the same: 25 g of succinimide with mp 126° C, 150 g of solvent, and 2.5 g of catalyst. The Raney nickel was prepared by a published method [10] and was washed with the corresponding alcohol before use. The residual content of aluminum in the catalyst was 24.1% and its specific surface (from the thermal desorption of argon) was 54 m^2/g. The catalyst was used only once. All the solvents were rendered absolute. The contents of pyrrolidinone and and succinimide in the samples taken were determined. The analyses were carried out on a UKh-1 chromatograph with a thermal conductivity detector. The conditions of the chromatographic separation were: column 1.7 m long and 3 mm internal diameter, column temperature 190° C, rate of flow of the carrier gas (helium) 90 ml/min. The polyester of butane-1,4-diol and succinic acid deposited on INZ-600 brick calcined at 1100° C was used as the liquid phase. An internal standard, sulfolane, was used for quantitative determinations of compositions of mixtures. The error of the method was ±5% rel. Since the vapor pressures of the solvents used differed considerably from the vapor pressures of succinimide and pyrrolidinone, the results of the analyses were corrected by comparison with the concentrations of pyrrolidinone in samples taken from the autoclave under normal conditions and under the experimental conditions.

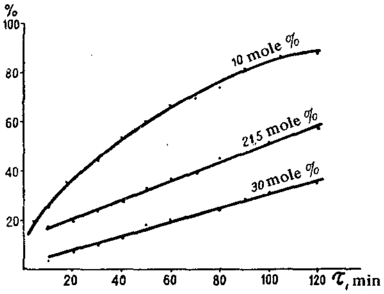

Fig. 3. Absorption of hydrogen (%) at various initial concentrations of succinimide in dioxane.

The results obtained are given in Tables 1 and 2 and Figs. 1–3.

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