Hydrogenation of Furfurylamine to 2,5-Dipropylpiperazine and Piperidine

JOHN BRAMMER PETERSEN* and KJELD NORRIS**

28 Rugmarken, Farum, Denmark

The transformation of furfurylamine into piperidine by catalytic hydrogenation has been reported twice in the literature.

Schmidt, Blaser and Manchen [1] obtained piperidine in good yields (yields not specified) when heating furfurylamine with hydrogen, ammonia, and various catalysts under pressures above 50 atmospheres and at temperatures above 200°. Wilson,[2] under similar conditions, using Raney nickel, but no ammonia, obtained a 9 % yield of piperidine together with 43 % of *N*-tetrahydrofurfurylpiperidine.

We have hydrogenated furfurylamine catalytically under 100 atmospheres at 300° and obtained piperidine (11 %) and 2,5-dipropylpiperazine (24 %). Our reaction does not proceed *via* tetrahydrofurfurylamine, since this compound was recovered unchanged after treatment under the same reaction conditions.

2,5-Dipropylpiperazine is new. Its structure was proved by analysis and comparison with a sample prepared by hydrogenation of 3,6-dipropyl-2,5-piperazinedione (*cf.* Ref. 3).

Experimental. Hydrogenation of furfurylamine. Furfurylamine (30.0 g, 0.31 mole) and copper-chromium oxide (2.00 g) (catalyst G22 from Girdler-Südchemie Katalysator GmbH, München, Germany) were shaken under hydrogen (100 atm.) in a 500 ml glass-lined autoclave at 300° for one hour. The quantity of hydrogen absorbed was 0.84 mole. After being cooled to zero the reaction mixture (odour of ammonia) was filtered. The filtrate was mixed with a filtrate from an identical experiment and the mixture distilled through a short 10-plate column under atmospheric pressure. 20 ml of distillate, b.p. 80–99°, was collected.

The residue from the distillation crystallized on cooling. The crystals were isolated by filtration, washed with cold petroleum ether and dried. 2,5-Dipropylpiperazine (12.61 g, 24 %) was hereby obtained as white hygroscopic crystals, m.p. 84° (Hershberg app., corr.) Crystallization from petroleum ether (60 ml) gave 9.45 g, m.p. 87–88°. Further crystallization did not change the melting point. [Found: C 70.7; H 13.0; N 16.3. Calc. for $C_{10}H_{22}N_2$ (170.2): C 70.6; H 13.0; N 16.5]. The product was in every respect identical with a sample prepared by hydrogenation of 3,6-dipropyl-2,5-piperazinedione.[3]

The 20 ml portion of the distillate was dried with solid potassium hydroxide and redistilled. Piperidine (5.88 g, 11 %), b.p. 90–105° (main portion 104°), was hereby collected. The product was further characterized by its toluenesulfonamide derivative and by gas chromatographic analysis.

2,5-Dipropylpiperazine dihydrochloride was prepared in the usual way. [Found: C 49.5; H 10.0; Cl (ionic) 29.4; N 11.5. Calc. for $C_{10}H_{24}Cl_2N_2$ (243.1): C 49.3; H 10.0; Cl 29.2; N 11.5].

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Kinetic Equations Assuming two Sets of Active Sites on a Catalyst

STEIN KOLBOE

Central Institute for Industrial Research, Oslo 3, Norway

Recently Shah and Davidson [1] published an article exploring the possibility that it may be necessary to assume more than one rate determining step in the kinetic equations of the Hougen-Watson type [2] for a heterogeneously catalyzed gas phase reaction. An equation taking into account that both surface reaction and desorption

* Present address: Rexolin Chemicals AB, Hälsingborg, Sweden.

** Present address: The Weizmann Institute of Science, Rehovoth, Israel.

are rate limiting processes [3] was applied to kinetic data for the initial rates (no influence of products) of the dehydrogenation of sec-butyl alcohol over a brass catalyst.[4] This reaction had previously been shown to deviate from the behaviour predicted by the Hougen model, and it seemed necessary to assume a transition from one rate controlling step to another with increasing temperature.[4,5] The kinetic data may be explained in a different way, however, which has surprisingly been overlooked so far, when interpreting kinetic results in catalysis. A preliminary account is given here.

The kinetic equations of Hougen and Watson [2] are based on the assumption that there is only one type of active sites. Hence for a surface reaction controlled mechanism involving n centers we have at zero conversion

$$r = \frac{k\,a\,p}{(1 + ap)^n} \qquad (1)$$

where r is the reaction rate (moles per second, and mass or surface unit of catalyst). k is the rate constant and a is an adsorption constant. Several reasons may be advocated for assuming that in general there are two or more sets of active centers. These reasons will not be given here, but if we do assume the catalyst to consist of two different sets of centers, eqn. 1 is transformed into

$$r = \frac{k_1\,a_1\,p}{(1 + a_1p)^n} + \frac{k_2\,a_2\,p}{(1 + a_2p)^n} \qquad (2)$$

Applying eqn. 2 to the set of data given by Thaller and Thodos [4] for $t = 600°F$ by carrying out a least squares parameter estimation an excellent fit is obtained. Choosing $n = 3$, one obtains parameter estimates, $k_1 = 0.1805$, $a_1 = 1.2671$, $k_2 = 0.2646$, $a_2 = 0.1017$ and a mean percentage deviation of 2.53 % corresponding to 4.31 % per degree of freedom. The mean residual square per degree of freedom is 2.342×10^{-6}.

This mean residual square is probably not larger than the experimental variance, thus the bias of the curve may be zero. Eqn. 2 may therefore possibly give a complete description of the reaction, although lack of bias does not imply correctness of the model and a bias may occur in other experimental regions of the system. When appropriate, all other kinetic equations of the Hougen type may of course be transformed into sums in analogy with the transformation of eqn. 1 into eqn. 2.

A complete description of the work will appear shortly.

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Influence of γ-Irradiation on β-Fructofuranosidase in Potato Tubers

MAIRE JAARMA

Biokemiska institutionen, Kungl. Universitetet i Stockholm, Stockholm, Sweden

As early as 1903 Kastle and Clark [1] detected β-fructofuranosidase ("invertase") in potato tubers. These authors reported that "invertase" was found only in sprouted, but not in unsprouted, tubers, an observation later confirmed also by McCready.[2]

Denny *et al.*[3] found that the "invertase" activity of potato juice from tubers treated with a sprout inhibitor was greater than that from the juice of untreated tubers. The sprouting of the tubers is irreversibly inhibited by suitable doses of γ-irradiation; thus, it seems obvious to assume that the activity of the "invertase" in the tubers would be influenced also by irradiation.

In order to investigate whether this hypothesis could be confirmed, crude "invertase" preparations were isolated from irradiated and non-irradiated potato tubers, and enzyme activities of these preparations were determined.