PIPERIDINE-MODIFIED FISCHER–TROPSCH SYNTHESIS

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N-Alkylpiperidines with alkyl fragment length from C_1 to C_{15} were synthesized by the reaction of CO + H_2 + piperidine. The molecular mass distribution of the N-alkylpiperidines has two different distribution parameters α. Thus, $\alpha = 0.45 \pm 0.03$ for C_1-C_5 alkyl fragments, while $\alpha = 0.65 \pm 0.02$ for C_6-C_{15}. Piperidine was found to act as a modifier reagent and chemical trap for the intermediates in the synthesis reaction.

The modification of reactions based on mixtures of carbon monoxide and hydrogen or water, proceeding in the presence of iron catalysts, by the addition of ammonia or various amines markedly expands the scope of Fischer–Tropsch (1) [1-3] and Kolbel–Engelhardt reactions (2) [4-6]:

$$n\mathrm{CO} + 2n\mathrm{H_2} + \mathrm{R^1R^2NH} \rightarrow \mathrm{C_nH_{2n+1}NR^1R^2} + n\mathrm{H_2O}, \quad (1)$$

$$3n\mathrm{CO} + n\mathrm{H_2O} + \mathrm{R^1R^2NH} \rightarrow \mathrm{C_nH_{2n+1}NR^1R^2} + 2n\mathrm{CO_2}, \quad (2)$$

$\mathrm{R^1}, \mathrm{R^2} = \mathrm{H}$, Me, n-Bu.

The introduction of modifying additives such as ammonia, primary or secondary amines directly into syntheses using CO and H_2 (or H_2O) permits the preparation of various amines in addition to the usual hydrocarbon, alcohol, and ketone products. Furthermore, the use of a modifying reagent permits us to refine various aspects of the mechanism of these reactions. In this regard, undoubted interest is found in the behavior of heterocyclic amines such as piperidine under the conditions of the Fischer–Tropsch reaction. Such a method for the preparation of N-alkylpiperidines has been reported relative to the Kolbel–Engelhardt reaction [7]. The possibility of carrying out such a reaction under the conditions of the Fischer–Tropsch synthesis has not been elucidated.

In the present work, we studied the transformation of piperidine upon its reaction with synthesis gas on a reduced promoted fused iron catalyst (RPFIC).

EXPERIMENTAL

The experiments on the syntheses using CO, H_2, and piperidine were carried out in a flow reactor with a fixed catalyst bed, analogous in composition to that described in our previous work [1,2]. The reaction was carried out in the gas phase at 180-185°C. The pressure of the synthesis gas was 12 MPa ($H_2/CO = 2$). The volumetric rate of the gas mixture was $1.5 \cdot 10^3$ h^{-1}. The piperidine partial pressure was varied from 0.03 to 0.05 MPa. Under these conditions, the CO conversion ranged from 15 to 20%. The desired amines were removed from the anhydrous portion of the liquid products at 20°C by treatment with a mixture of one part water and one part concentrated hydrochloric acid and analyzed by gas-liquid chromatography on a Chrom-5 chromatograph equipped with a flame ionization detector using a 1200 × 3-mm column packed with 10% SE-30 on Chromosorb N-AW-DMCS (0.15-0.20 mm). The nitrogen flow rate was 30 cm^3/min. The temperature programming was from 50 to 300°C. The temperature was raised at a rate of 6°C/min. The components of the amine mixture were identified by GC/MS on a Kratos MS-25RF/DS-90 instrument at 70 eV using a 25 m × 0.35-mm quartz capillary

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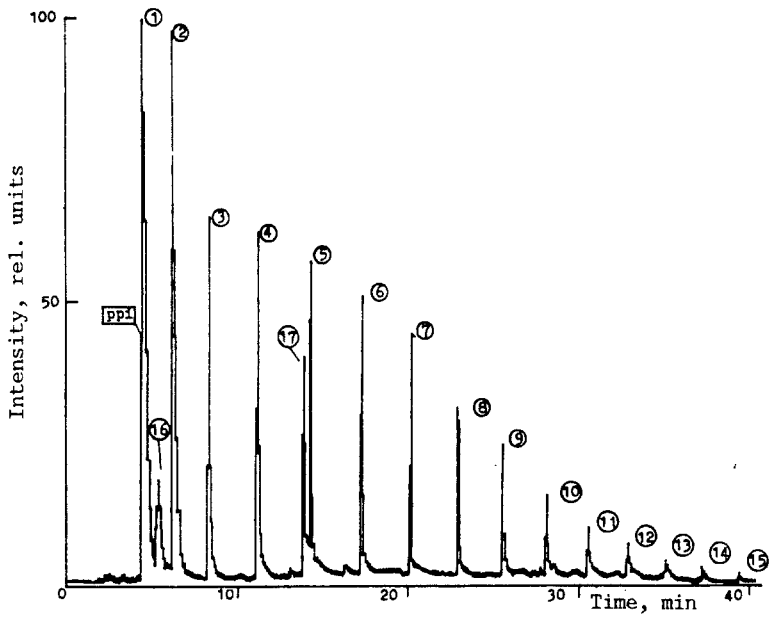


Fig. 1. Chromatograms for the amines isolated from the reaction of $CO + H_2 + C_5H_{11}N$: 1-15) N-alkylpiperidines with the general formula $C_nH_{2n+1}NC_5H_{10}$, where n = 1-15; ppi) piperidine, 16) 2-methylpiperidine, 17) 2-ethylpiperidine.

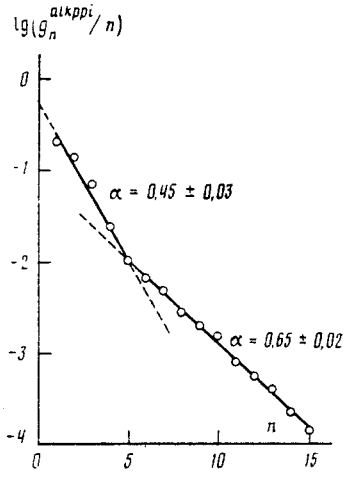


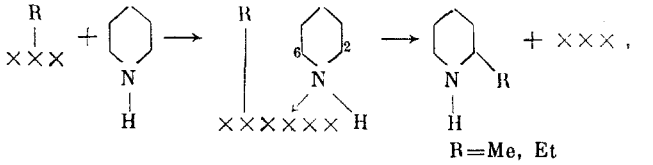
Fig. 2. Molecular mass distribution of N-alkylpiperidines (aklppi) in a semilog plot of the Shul'ts equation $\log(g_n^i/n) = \log(\ln^2 \alpha) + n\log \alpha$.

column packed with SE-30. The emission current was 50 μA. The temperature of the ion source and molecular separator was 200°C. The temperature programming was from 50 to 280°C and the temperature was raised at a rate of 10°C/min.

RESULTS AND DISCUSSION

A study of the condensed products of the synthesis from carbon monoxide, hydrogen, and piperidine obtained under the conditions described above showed that they contain 60-70% N-alkylpiperidines. The nonamine fraction contains 10-15% normal alcohols, 5-10% carbonyl compounds with the remainder consisting of normal alkanes and alkenes with a terminal C=C bond. The overall yield of the synthesis products was 130-140 g per 1 m^3 converted synthesis gas ($H_2/CO = 2$).

A typical chromatogram of the synthesized alkylpiperidines is given in Fig. 1. These data show that the major components of the amine mixture obtained are N-alkylpiperidines with the general formula $C_5H_{10}NC_nH_{2n+1}$, where n = 1-15. We should especially note the presence of 3% 2-methylpiperidine and 2% 2-ethylpiperidine. This finding may be attributed to alkylation of the piperidine in the ring by surface methyl and ethyl intermediates initially obtained from carbon monoxide and hydrogen. The formation of only 2-alkylpiperidines is probably a consequence of the adsorption of the piperidine molecule at the acid–base sites of the iron catalyst [3] through the nitrogen atom such that C^2 and C^6 become most accessible for reaction with the surface intermediates.



where XXX is the catalyst surface.

Since the concentration of the surface intermediates and of the products from these intermediates steadily drops off with increasing length of the hydrocarbon chain in accord with the Shul'ts–Flory law [8], the formation of other 2-alkylpiperidines is unlikely.

Thus, the piperidine added to synthesis gas acts as a modifying reagent and chemical trap for the surface intermediates. We thereby show that saturated nitrogen heterocyclic compounds may be used as chemical traps for intermediates. Previously, ring alkylation was observed upon the introduction of only pyridine into the Fischer–Tropsch synthesis [9,10].

Figure 2 gives the molecular mass distribution of the N-alkylpiperidines synthesized in a semilog plot of the Shul'ts equation and shows that the experimental results are in satisfactory accord on two lines with different slopes, intersecting at n = 5. The distribution parameter α for the range from N-methylpiperidine to N-pentylpiperidine is 0.45 ± 0.03, while α for the range from N-hexylpiperidine to N-pentadecylpiperidine is 0.65 ± 0.02. This discontinuity in the distribution lines is observed for the first time in modified Fischer–Tropsch syntheses. Previously, such behavior was found only for the hydrocarbon fraction of the product of the synthesis from carbon monoxide and hydrogen on fused iron catalysts and was attributed to the formation of alkanes on two different types of active sites [11].

Taking account of the hypothesis of Huff and Satterfield [11] relative to our results, we should postulate the formation of N-alkylpiperidines with alkyl fragment length up to C_5 on one type of sites and the remainder on different active sites. Such selectivity may be explained, for example, by the existence of steric limitations to growth of the hydrocarbon chain within each type of catalyst active site.

It is interesting to note that the distribution parameter was 0.5 ± 0.1 in the molecular mass distribution of the products of the unmodified Fischer–Tropsch synthesis on the same catalysts for the gaseous (C_1-C_5) fraction [8], while this parameter was 0.66 ± 0.02 for the condensed fraction (C_6-C_{20}) [11]. This circumstance indicates that the introduction of piperidine does not alter the molecular distribution of the synthesis products and such an approach may be used to reveal the true nature of the distribution of the actual products in a broad fraction.

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SYNTHESIS OF 1,3-DIHALO-1,3-DIOXIMINO-2-PROPANONES

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1,3-Dihalo-1,3-dioximino-2-propanones (Hal = Cl or Br), which had been difficult to prepare or unreported, were obtained by the nitrosation of 1,3-dihalo- and 1,3-dihalo-1-oximino-2-propanones by nitrosylsulfuric acid in concentrated H_2SO_4.

Reactive hydroxamic acid chlorides have found common use in organic synthesis, in particular, in the synthesis of heterocycles such as furoxanes, oxazolines, and 1,2,4-oxadiazoles [1-4]. This has led to a search for new methods for the preparation of such compounds. Dihydroxamic acid chloride derivatives have synthetic value as polyfunctional compounds with two reactive groups. For example, 1,2-dichloro-1,2-dioximinoethane (dichloroglyoxime) has found various synthetic uses [5]. However, the range of such difunctional derivatives is extremely limited.

In the present work, we studied the possibility of obtaining 1,3-dihalo-1,3-dioximino-2-propanones, which are dihydroxamic acid chlorides containing an additional carbonyl function.

The literature data on the preparation of such derivatives are very sparse. Bateman [6] has described the synthesis of 1,3-dichloro-1,3-dioximino-2-propanone (I) by the action of a six-fold excess of NaOCl on acetone in dry ether over two weeks. The reaction details as well as the yield and properties of (I) (except for its melting point) were not given by this worker. We isolated only traces of (I) upon attempting to reproduce the synthesis of Bateman [6]. Kanungo et al. [7] has reported the synthesis of 1,3-dibromo-1,3-dioximino-2-propanone (II) by the bromination of 1,3-dioximino-2-propanone in aqueous alkali. We were unable to find the specific details for the preparation of (II) and the indices of this compound.

In order to obtain (I) and (II), we studied the nitrosation of available 1,3-dichloro- and 1,3-dibromo-2-propanones by various nitrosating reagents. The acidic nitrosation of ketones proceeds through attack of the nitrosating agent on the enol form. The presence of an electron-withdrawing substituent in the α-position to the carbonyl group markedly reduces the tendency to undergo enolization. This probably accounts for the failure of the nitrosation of 1,3-dichloro- and 1,3-dibromo-2-propanones using $NaNO_2$ in hydrochloric acid and i-PrONO in ether saturated with HCl as the nitrosating agents. The nitrosation of 1,3-dichloro-2-propanone to give (I) was achieved only using nitrosylsulfuric acid in concentrated H_2SO_4. The mononitrosation product, namely, 1,3-dichloro-1-oximino-2-propanone (III) (Scheme 1) is obtained upon reduction of the acidity of the reaction medium by the addition of glacial acetic acid. The properties of our sample of (III) corresponded to the data reported by Kurtz [8].

The nitrosation of 1,3-dibromo-2-propanone under conditions analogous to the conditions for the synthesis of (I) proceeds to give not only (II) but also the mononitrosation product, namely, 1,3-dibromo-1-oximino-2-propanone (IV) and 3,5-dibromo-4H-pyrazol-4-one N,N'-dioxide (V) (Scheme 2) as indicated by thin-layer chromatography. This dioxide is formed, in all likelihood, by the oxidative cyclization of (II). The formation of analogs

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