TRACER STUDY OF TOLUENE FORMATION IN THE HYDROGENOLYSIS OF HEXANE ON NICKEL CATALYST

L. Guczi, J. Kálmán and K. Matusek
Institute of Isotopes of the Hungarian Academy of Sciences,
Budapest, Hungary

Received: July 19, 1973

The possible routes of toluene formation in the hydrogenolysis of n-hexane on nickel catalyst have been investigated by a tracer technique. The direct alkylation process seems to occur and toluene formation via disproportionation may be excluded.

ИЗУЧЕНИЕ ФОРМИРОВАНИЯ ТОЛУЕНА ПРИ ГИДРОГЕНОЛЗИЗЕ Н-ГЕКСАНА НА НИКЕЛЕВОМ КАТАЛИЗАТОРЕ

Возможные пути реакций образования толуола в гидрогенолизе n-гексана на никелевом катализаторе были исследованы с помощью радиоактивной техники. Кажется вероятным процесс непосредственного алкилирования, а образование толуола через диспропорционирование может быть исключено.

INTRODUCTION

The formation of toluene in the reaction of n-hexane on Pt and Pd ribbon was first observed by Gryaznov and co-workers [1, 2] at low temperatures and in the absence of hydrogen. Traces of toluene were obtained in hexane and heptane dehydrocyclization on Ni/alumina catalysts also without hydrogen [3, 4].

Earlier we have reported the formation of toluene over a non-supported nickel catalyst in the presence of hydrogen [5]. It was established that during the hydrogenolysis of n-hexane the amounts of benzene and toluene parallel each other and this tempted us to assume that toluene is formed directly via benzene alkylation with monocarbon fragments on the surface. The attractive idea of alkane disproportionation offered another pathway to explain the formation of toluene [6]. According to this idea, the first step is dehydrogenation and this is followed by disproportionation and eventually ring closure to form toluene.
The application of labelled benzene offers a possibility to distinguish between these two pathways. Namely, a comparison of the specific radioactivity of benzene admixed in a small amount to the hydrogen-hexane mixture with that of the toluene formed helps to decide between the two mechanisms.

EXPERIMENTAL

The catalytic apparatus, the preparation of the catalyst and the experimental procedure have been described [7]. In some experiments an MS 10 mass spectrometer was used to analyze the products of the reaction. The tracer experiments involving benzene labelled with carbon-14 were (specific radioactivity 0.32 Ci mol\(^{-1}\)) carried out in the same apparatus but the analysis was made in a different way. A Packard Model 419 gas chromatograph was applied for the separation of the reaction products. The gas stream leaving the column (6 m in length, filled with 10% squalan on celite) was split into two parts: one was led to the FID to determine the quantity of the products and the other was used for radioactivity measurements. The latter were performed - after passing the effluent gas over heated CuO to convert all hydrocarbons to CO\(_2\) - by means of a proportional flow counter. Before entering the counter, the argon carrier gas was mixed with about an equal amount of methane. The specific radioactivity of the different components was calculated according to the ratio of the radioactivity of the sample divided by its amount.

RESULTS AND DISCUSSION

The formation of toluene was observed first in the mass spectrometer, using 91 mg of a Ni catalyst (surface area 3.6 m\(^2\) g\(^{-1}\)) on which experiments with hydrogen to n-hexane ratios of 11.2 and 3.2 (initial amount of n-hexane 2.7 x 10\(^{-5}\) mol) were carried out. Typical runs are presented in Fig. 1 where the amounts of benzene and toluene are plotted against time at 242 and 289 °C for different hydrogen to n-hexane ratios. It seems that the amount of cyclic products increases with the temperature. At the higher ratio, however, these products undergo fast hydrogenolysis, therefore, their concentrations pass through maxima. Especially in this latter case, the parallelism between the curves of benzene and those of toluene is striking. This parallel-