

Special Custom Translation

CHF

The Effect of Hydrogen Pressure in the Rate and Direction of the Homogeneous^e Destructive Hydrogenation of Alkylbenzenes.

M. G. Gonikberg and V. E. Nikitenkov.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. (Presented by Academician B. A. Kazanskii, Jan. 29, 1955) Translated from Doklady Akademii Nauk SSSR, Vol. 102, No. 5, pp. 949-952, 1955. Original article submitted Jan. 26, 1955.

It is known that the rate and direction of homogeneous^e destructive hydrogenation of alkylbenzenes is substantially dependent on hydrogen pressure. An increase in hydrogen pressure in the homogeneous^e destructive hydrogenation of ethylbenzene leads to an increase in the benzene content and a decrease in the toluene content of the reaction products /1/. This fact, and other analogous data are sometimes interpreted as the relative weakening under hydrogen pressure, of the $C_{\text{aliph}}-C_{\text{arom}}$ bond in alkylbenzenes. But it is evident that hydrogen pressure (of the order of several hundreds of atmospheres) cannot in any way significantly change the relative strength of these or any other chemical bonds (or the absolute value of the bond energies). Discussion here therefore centers on the difference in the mechanisms of thermal degradation and of the homogeneous destructive hydrogenation of alkylbenzenes.

9) In the studies which we carried out earlier on the homogeneous destruction^{ve hydrogenation} of toluene under high hydrogen pressure /2/ (as

well as in the earlier publication /1/) it was pointed out that demethylation of toluene is significantly accelerated with increasing hydrogen pressure. In our paper /2/ we proposed a chain-reaction mechanism for this process. Basic to this scheme is the reaction of radical^s, formed in the thermal degradation of tolueneⁿ, with hydrogen (and with molecules of toluene and with reaction products). The reaction with H₂ molecules generates atomic hydrogen. The latter, in turn, attacks toluene molecules /3,4/ with the formation of methane and phenyl radicals, or benzene and methyl radicals (or possibly, also tolyl radicals) and the chain reaction continues in the same manner. It is precisely this reaction of atomic hydrogen with alkylbenzene molecules, which is apparently responsible for the change in composition of the products of the homogeneous destructive hydrogenation with increased hydrogen pressure. Thus, for ethylbenzene, one might expect the following reaction *

*(Footnote R.p. 949) We have noted only the chain-initiation reaction and some chain-propagation reactions involving hydrogen.

.....R. p. 949

Reaction (1) appears to be the first step in the thermal degradation of ethylbenzenes (see /5/).

.....R. p. 949

.....R. p. 950

The molecules of toluene formed in this process undergo further transformation into benzene and methane /2/.

Apparently chain termination occurs mainly by radical recombination. Examination of equations (1) - (6) leads to the conclusions that with increased concentration, and therefore, with increased pressure of hydrogen, benzene formation should be accelerated; that the formation of toluene should be significantly limited by the rate of reaction (1)*;

*(Footnote R.p. 950) The possibility is not excluded that toluene formation may result from the reaction , but the relative probability of such a reaction is small /5/.

and that demethylation of toluene should also be accelerated by increased hydrogen pressure. In this way one can elucidate the effect of hydrogen pressure on the rate and course of homogeneous destructive hydrogenation of ethylbenzene.

We were interested in studying the effect of hydrogen pressure on the course of the process of destructive hydrogenation of isopropylbenzene, whose thermal decomposition yields a variety of products (hydrogen, methane, ethane, ethylene, propane, propylene, butane, benzene, toluene, xylenes, ethylbenzene, n-propylbenzene, styrene, α -methylstyrene, etc.) /6-10/.

As was shown in publication /10/, the first step in the thermal degradation of isopropylbenzene is the reaction

.....R. p. 950

In homogeneous destructive hydrogenation the further reactions involving the participation of hydrogen, are

.....R. p. 950

The ethylbenzene which is formed undergoes further destructive hydrogenation.

As indicated above, the exptl. studies of the pyrolysis of ethylbenzene and of isopropylbenzene lead to the conclusion that it is the rupture of the C-C bond in the side chain, and not of the $C_{arom} - C_{aliph}$ bond, which constitutes the first step in the process of thermal decomposition of these hydrocarbons. This is confirmed by data on bond dissociation energies. According to the calculations of N. N. Semenova /11/, the dissociation energy of the C-C bond in $C_6H_5-CH_3$ is equal to 87.5 kcal/mole, and that of the C-C bonds in is equal to 84.6 kcal/mole. The dissociation energy of the C-C bonds in the side chains of alkylbenzenes is significantly smaller, about 57.5-65.0 kcal/mole.

Let us now consider our exptl. data.

Our investigation which was carried out under autoclave conditions at 475° and at working pressures up to 680 atm (initial hydrogen pressures of 50-300 atm) showed the overall conversion of isopropylbenzene was accelerated with increasing hydrogen pressure. Thus, after three hours this conversion was 71% at 300 atm working pressure, about 80% at 390 atm and about 90% at 670 atm. The composition of the liquid reaction products undergoes a very substantial change. When the duration of the expt. was three hours, and the working pressure was 180-220 atm, the benzene content of the reaction products corresponded to 8-9 wt. % of the isopropylbenzene initially charges^d; at 300 atm, it was 20-22%; at 670 atm it was 46-49%. The toluene contents under these conditions were, respectively,

11-13, 7-8 and 2-3%; while the ethylbenzene contents were 19-20, 14-15 and 2-5%.* Thus, an increase in hydrogen pressure sharply

* (Footnote, R.p. 951) In liquid products boiling below 160°, the overall content of paraffinic, naphthenic and olefinic hydrocarbons did not exceed 1%.

increases the yield of benzene and reduces the yield of toluene and ethylbenzene.

However the data on the composition of the liquid products are insufficient to verify the above-described schematic mechanism for the homogeneous destructive hydrogenation of alkylbenzenes. Analogous changes in the composition of the liquid reaction products with increasing hydrogen pressure might, in principle, occur if it were assumed that hydrogen pressure accelerated the degradation of isopropylbenzene to ethylbenzene, from ethylbenzene to toluene, and from toluene to benzene, even if benzene were not formed from ethylbenzene by reactions (4)-(5) or from isopropylbenzene by reactions (9) and (5).

Obviously, in the latter case, the gaseous products of the reaction at any hydrogen pressure would be predominantly methane while the course of the reaction by equations (7)-(10) should lead to an increase in propane content and a reduction of the methane content in the gaseous products at increasing hydrogen pressure. Analysis of the gaseous reaction products does, in fact, indicate a significant increase in their propane contents. Fig. 1 shows the change in the ratio** with

** (Footnote R.p. 951) The quantities in parentheses are molar concentrations.

increasing pressure at 475° at an exptl. duration of three hours. It was shown that under the indicated conditions this ratio increases with pressure. (It is approximately proportional to the initial hydrogen pressure).

Fig. 1. Effect of initial hydrogen pressure on the ratio at 475° ($t=3$ hours).

(key)

1) atm

2) initial

Fig. 2 shows the dependence of the ratio on the yield of benzene (in mole per cent) to the overall yield of toluene and ethylbenzene as a function of the initial hydrogen pressure at 475° for different exptl. durations.

Fig. 2. Effect of initial hydrogen pressure on the ratio (benzene): [(toluene)+(ethylbenzene)] at 475° . a - 2 hours, b - 3 hours, c - 4 hours, d - 5 hours.

(key)

1) a

2) b

3) c

4) d

5) initial

6) atm²

It appears that this ratio, at $t=2,3,4$ and 5 hours in the range of initial hydrogen pressures of 0-200 atm increases nearly proportionately to the square of the pressure.

Thus, increase in hydrogen pressure in the homogeneous destructive hydrogenation of isopropylbenzene significantly increases the yields of benzene and propane, compared to the yields of other liquid and gaseous reaction products. The fact that the (benzene):(toluene + ethylbenzene) ratio (Fig. 2) increases with increasing hydrogen pressure to a greater extent than does the ratio (propane):(ethane + methane) (Fig. 1), is easily explained. Benzene is formed directly from isopropylbenzene as well as from ethylbenzene and toluene, the yields of which decrease with increasing hydrogen pressure. In contrast to benzene, propane is formed only from isopropylbenzene. Recombination of methyl and ethyl radicals to form propane proceeds apparently to a negligible degree* and, in

*(Footnote R.p. 952) Thermal degradation of isopropylbenzene yields gaseous products containing methane and ethane, but almost no propane.

any case slows down rather than accelerates, with increasing hydrogen concentration.

The results of this study support the description, given in this paper, of the mechanism of homogeneous destructive hydrogenation of alkylbenzenes.

LITERATURE CITED

1. M. S. Nemtsov, Usp. Khim. 7, 1617 (1938).
2. M. G. Gonikberg and V. E. Nikotenkov, Izv. AN SSSR, OKhN, 936 (1954).
- 3-5
6. A. F. Dobryanskii, E. K. Kanep and S. V. Katsman, Proceedings of "Khimgaz" plant (in Russian) 3, 1 (1936).
- 7-10
11. N. N. Semenov, Some problems in chemical kinetics (in Russian) Izv. AN SSSR, 1954, p. 27.