

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Simultaneous Dehydrogenation-Hydrogenation of Cyclohexene in the Presence of Nickel

BY B. B. CORSON AND V. N. IPATIEFF

Cyclohexene is catalytically converted into a mixture of cyclohexane and benzene,¹ $3C_6H_{10} \rightarrow 2C_6H_{12} + C_6H_6$, as shown by Böeseken and Sillevs² who used platinum and nickel as catalysts. Later, Zelinskii and Pavlov³ studied the catalysis of this reaction by platinum and palladium.

Böeseken and Sillevs used nickel at 180° but the refractive index of their product (n_D^{20} 1.4631) was not that of a mixture of two mols of cyclohexane plus one mol of benzene (n_D^{20} 1.4445). Zelinskii⁴ reported incomplete conversion with a nickel-alumina catalyst at 110° and also at 180°.

The foregoing work would indicate that nickel is not an effective catalyst for this reaction. We have found, however, that nickel is an excellent catalyst, both at superatmospheric pressure (which has not been employed previously) and at ordinary pressure. Under mild conditions the liquid product is the mixture of 68% by weight of cyclohexane and 32% of benzene corresponding to the above equation. Small amounts of hydrogen and methane are formed. Under superatmospheric pressure, with a reaction time of six hours at temperatures from 100 to 400° the hydrogen production is only 0.04 to 0.4 liter per mole of cyclohexene but the amount of methane increases from 0.3 liter at 100° to 16 liters at 400°. The yield of methane at 400° corresponds to a 6% conversion of the carbon of the initial cyclohexene. The liquid product becomes richer in benzene with increasing temperature. At 400° the composition is 46% cyclohexane and 54% benzene. In the absence of nickel catalyst, and using a clean steel autoclave equipped with a glass liner, cyclohexene is practically unchanged by heating for six hours at 350°, and only 7% by heating for six hours at 400°. At ordinary pressure, in the vapor phase, the conversion of cyclohexene to cyclohexane and

benzene is practically quantitative at 75° in a contact time of fifteen seconds and at 100° in one second.

Experimental

Analytical Procedure.—The liquid product was distilled to free it from the small amount (trace to 2%) of high boiling material which was always formed. In the absence of olefin, as shown by permanganate test and bromine number, the amounts of cyclohexane and benzene were estimated from the refractive index. The weight percentage composition of a mixture of 2 moles of cyclohexane and 1 mole of benzene is 68.3% of the former and 31.7% of the latter; its n_D^{20} is 1.4445. Analysis of the liquid with cold 15% fuming sulfuric acid checked the refractive index estimate within 1 to 3%. A complete Göckel analysis was run on the gas.

Apparatus, Procedure, and Materials

The superatmospheric batch experiments were made in a 3515-cc. stainless steel rotating autoclave of the Ipatieff type.

The atmospheric continuous runs were made in a glass tube which was heated in a vertical furnace. Cyclohexene was charged into the upper end of the tube by means of an electric micro-pump.⁵ The liquid product was collected in an ice-cooled receiver attached to the lower end of the tube by a ground glass joint. The exit gas was collected over water. At the end of a run the receiver was allowed to stand one hour at room temperature and the disengaged gas was collected with the rest of the gas sample. The gas sample taken for analysis was passed through an ice trap to remove non-gaseous material. The contact time in seconds of the cyclohexene in the catalyst chamber was calculated as free space divided by gas rate per second at the reaction temperature.

The cyclohexene was freshly distilled Eastman product. The nickel catalyst⁶ consisted of about 65% of nickel and 35% of kieselguhr and had been fabricated in the form of $\frac{1}{8} \times \frac{1}{8}$ (3.2 \times 3.2 mm.) pills. The catalyst volume was 85 cc. (100 g. of catalyst) with a free space of 54 cc.

Superatmospheric Batch

Cyclohexene with Nickel.—The charge was 100 cc. of cyclohexene, 10 g. of nickel catalyst, and 10 kg./sq. cm. of nitrogen. The bomb was rinsed with nitrogen to displace the air. The reaction time was six hours. The liquid recovery was 90–95%. The distilled product was stable to permanganate and gave *m*-dinitrobenzene with nitrating mixture except in the case of the 100° experiment in which the product was unchanged cyclohexene. The residue remaining after treatment with cold 15% fuming sulfuric acid was cyclohexane (n_D^{20} 1.4260–1.4265).

(5) Tropisch and Mattox, *Ind. Eng. Chem.*, **26**, 1338 (1934).

(6) Ipatieff and Corson, *ibid.*, **30**, 1039 (1938).

(1) This mixture of cyclohexane and benzene was mistaken by Zelinskii [*J. Russ. Phys.-Chem. Soc.*, **43**, 1222 (1911)] for a "new tetrahydrobenzene." He obtained it by passing cyclohexene over palladium black.

(2) Böeseken and Sillevs, *Verslag. Akad. Wetenschappen*, **22**, 441 (1914); Böeseken, Groot and Jzn, *Rec. trav. chim.*, **37**, 255 (1918); cf. Padoa and Fabris, *Atti Accad. Lincei*, [5] **17**, ii, 125 (1908).

(3) Zelinskii and Pavlov, *Ber.*, **56**, 1249 (1923); **57**, 1066 (1924); **66**, 1420 (1933).

(4) Zelinskii, *ibid.*, **57**, 2055 (1924).

TABLE I
CYCLOHEXENE WITH NICKEL

| T, °C. | n_D^{20} | Br no. | C ₆ H ₁₂ | C ₆ H ₆ | Gas Liters (N. T. P.) per mole of C ₆ H ₁₀ | |
|--------|------------|------------------|--------------------------------|-------------------------------|---|-----------------|
| | | | | | H ₂ | CH ₄ |
| 100 | 1.4463 | 191 ^a | 0 | 0 | 0.04 | 0.3 |
| 125 | 1.4461 | 0.2 | 68 | 32 | .04 | .3 |
| 150 | 1.4459 | .1 | 68 | 32 | .1 | .5 |
| 200 | 1.4462 | .1 | 68 | 32 | .1 | 1.2 |
| 250 | 1.4505 | .1 | 62 | 38 | .1 | 4.9 |
| 300 | 1.4553 | .1 | 54 | 46 | .4 | 10.2 |
| 350 | 1.4600 | .1 | 48 | 52 | .3 | 13.6 |
| 400 | 1.4610 | .6 | 47 | 53 | .0 | 16.0 |

^a Bromine number of original C₆H₁₀, 191.

Cyclohexene without Nickel.—The bomb was cleaned by wire-brushing followed by dilute hydrochloric acid and finally by steam. The cleaned bomb did not hydrogenate benzene at all in twelve hours at 350° under an initial hydrogen pressure of 100 kg./sq. cm. One hundred-cc. samples of cyclohexene were heated in this bomb for six hours at 200, 300, and 400°, and similar experiments were also made, using a glass liner with capillary glass stopper. Conversion was considerably less in the glass liner than in the steel bomb alone (Table II).

TABLE II

| CYCLOHEXENE WITHOUT NICKEL | | | | | | | | | |
|----------------------------|------------|--------|---|-----------------------|--------|---|-----------------------|--------|---|
| T, °C. | Bomb alone | | | Bomb plus glass liner | | | Bomb plus glass liner | | |
| | n_D^{20} | Br no. | Gas Liters (N. T. P.) /mole of C ₆ H ₁₀ | n_D^{20} | Br no. | Gas Liters (N. T. P.) /mole of C ₆ H ₁₀ | n_D^{20} | Br no. | Gas Liters (N. T. P.) /mole of C ₆ H ₁₀ |
| 200 | 1.4463 | 187 | 0 | 0.8 | | | 1.4463 | 191 | 0.5 |
| 300 | 1.4470 | 136 | 0.8 | 1.2 | 1.4463 | 191 | 0.5 | 3.0 | |
| 350 | | | | | 1.4463 | 188 | .2 | 1.8 | |
| 400 | 1.4540 | 0.8 | 5.2 | 0.4 | 1.4463 | 178 | .7 | 1.4 | |

Atmospheric Continuous

Cyclohexene with Nickel.—The yield of liquid product was practically quantitative. It was olefin-free. It contained benzene as shown by the formation of *m*-dinitrobenzene with nitrating mixture. The residue remaining after treatment with cold 15% fuming sulfuric acid was cyclohexane (n_D^{20} 1.4264–1.4266).

TABLE III
CYCLOHEXENE WITH NICKEL

| Conditions | T, °C. | C. T., sec. | Liquid | | Gas Liters (N. T. P.) per mole of C ₆ H ₁₀ | |
|------------|--------|-------------|--------|------------|---|--|
| | | | Br no. | n_D^{20} | Wt. % C ₆ H ₁₂ | Wt. % C ₆ H ₆ |
| 74 | 15 | 0.1 | 1.4458 | 68 | 32 | 0.2 |
| 100 | 1 | .1 | 1.4459 | 68 | 32 | .2 |
| 102 | 4 | .1 | 1.4460 | 68 | 32 | .3 |
| 152 | 5 | .2 | 1.4459 | 68 | 32 | .5 |

Cyclohexene without Nickel.—Cyclohexene was passed through a glass tube packed with glass rings at 97 and at 150°, the contact time being about thirty seconds. The product was unchanged cyclohexene: Br. no., 190, d_4^{20} , 0.811; n_D^{20} 1.4468.

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Summary

In the presence of nickel, both at superatmospheric and at ordinary pressure, cyclohexene is converted almost quantitatively into a mixture of cyclohexane (68% by weight) and benzene (32%).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Preparation of Cyclic Ketones by Ring Enlargement

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In response to a request from a group of physical chemists who are determining the heats of hydrogenation of unsaturated compounds¹ we have examined the feasibility of preparing a series of unsaturated cyclic hydrocarbons in sufficient quantity and of the unusual purity required for these physical measurements. The preparation of these compounds by methods based on ring closure appeared to us to be a hopeless undertaking because all of these methods fail almost completely in the case of compounds which have

from nine to eleven members in the ring and even with the best of these methods² it would be a formidable task to secure cyclooctanone in sufficient quantity to prepare cyclooctatetrene. We have, therefore, confined our attention to methods based on ring enlargement, and particularly to the reaction between ketones and diazomethane. Mosettig and Burger,³ who were the first to apply this reaction to carbocyclic ketones, added cyclohexanone to a standardized solution of diazomethane in ether and methyl alcohol. During the course of our work the reaction was employed in

* Due to the death of Professor Kohler, this manuscript was completed by his associates.

(1) Kistiakowsky, *et al.*, *THIS JOURNAL*, **60**, 440 (1938), and previous papers.

(2) Ziegler and Aurnhammer, *Ann.*, **513**, 57 (1934).

(3) Mosettig and Burger, *THIS JOURNAL*, **52**, 3456 (1930).