



metal oxide catalysts in vapor phase hydrogenation and dehydrogenation reactions. It is known that cycloolefins undergo a complete hydrogen disproportionation to cycloparaffins and aromatics on the surface of metal catalysts (*i.e.*, platinum, palladium and nickel).

In the present work, cyclohexene was subject to the action of pure vanadium trioxide at temperatures of 250–450° in an atmosphere of hydrogen and of nitrogen. The obtained results were compared with theoretical calculations.

Theoretical equilibrium concentrations of benzene and cyclohexane as a function of temperature were calculated from the equilibrium constants as presented by Rossini,<sup>2</sup> *et al.* Benzene and cyclohexane would be expected to form by one or more of three reactions, namely, hydrogenation, dehydrogenation or disproportionation. Figure 1 presents the theoretical concentrations of products from these reactions together with the experimental results. The theoretical concentrations were calculated on the basis of the initial partial pressure of cyclohexene being 0.12 atmosphere to that of hydrogen being 0.88 atmosphere, as used in this experimentation. It can be seen from Fig. 1 that, theoretically, hydrogenation would be the major reaction below 250°, both hydrogenation and dehydrogenation in temperature range 250–300° and dehydrogenation above 300°. The disproportionation reaction is possible throughout these temperatures. The experimental results have shown that cyclohexene in the presence of hydrogen, when passed at various temperatures (250–450°) over vanadium trioxide catalyst, shows no hydrogen disproportionation, but direct hydrogenation and dehydrogenation reactions approaching the theoretical values.

This fact is in line with the interpretation of edgewise adsorption of the organic molecule on the surface of metal oxide catalysts *versus* flat adsorption on the surface of metals.

#### Experimental Part

Cyclohexene (Eastman Kodak Co.) b.p. 82.5–83.5°,  $n_D^{20}$  1.4468, was vaporized in the stream of hydrogen at a constant rate into a glass tube filled with catalyst and placed in an electrically heated oven. The constancy of cyclohexene/hydrogen ratio (0.12:0.88 atmosphere) was maintained by a flowmeter (for hydrogen) and temperature of the evaporator (for cyclohexene). The liquid hourly space velocity was maintained between 0.015–0.017. The products were collected in receivers cooled with water and Dry Ice. Analysis was by distillation, chromatographic adsorption (silica gel) and determination of physical constants. The catalyst was prepared and activated as before.<sup>1</sup>

The experimental results are presented in Table I. It can be seen from the results obtained at lower temperatures that the activity of vanadium trioxide is extremely low. This was to be expected, since in the earlier work<sup>3</sup> with the same catalyst on hydrogenation of olefins its activity was at its maximum at higher temperatures (around 400°), which goes parallel with hydrogen adsorption and the amount of vanadium trioxide present. At higher temperatures the catalyst exhibits high activities and the reaction of dehydrogenation to benzene approaches the theoretical values. It is of importance for this discussion that in no case was there an excessive formation of cyclohexane and this consequently indi-

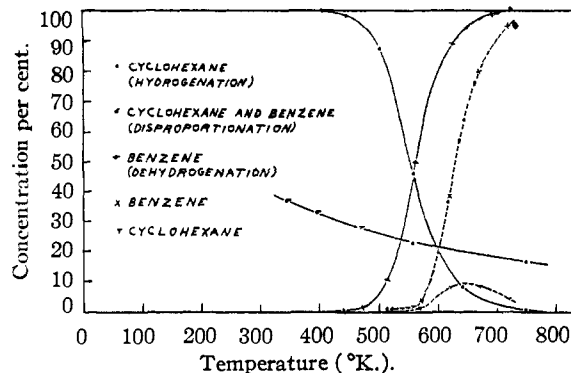


Fig. 1.—Reaction of cyclohexene and hydrogen. Theoretical equilibrium concentrations (solid lines) and experimental results (dotted line) over vanadia catalyst.

cates there is no hydrogen disproportionation reaction. Experiments carried out in an atmosphere of nitrogen showed similar results, the per cent. of dehydrogenation being somewhat higher than in experiments in hydrogen.

TABLE I

REACTION OF CYCLOHEXENE IN THE PRESENCE OF HYDROGEN AND OF NITROGEN (1:8 RATIO) OVER VANADIUM TRIOXIDE CATALYST. LIQUID HOURLY SPACE VELOCITY 0.015–0.017

Temp., °C.	$n_D^{20}$ of the product	Chromatographic analysis <sup>a</sup> of the product (%)		
		C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>10</sub>
A. Hydrogen experiments				
250	1.4465	98.5	1.5	0.5
300	1.4471	91.5	5.0	3.5
350	1.4583	53.8	38.5	7.7
400	1.4886	11.0	81.0	8.0
450	1.5010	0.0	97.0	3.0
B. Nitrogen experiments				
300	1.4473	100.0	0.0	0.0
350	1.4538	44.5	55.0	>0.5
400	1.4730	15.5	84.0	>0.5

<sup>a</sup> Initial boiling point of all products was 80° which clearly indicated that no isomerization to methylcyclopentane or methylcyclopentene took place.

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### The Reaction between Periodate and Cobaltous Ions<sup>1</sup>

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During a study of the determination of potassium as the metaperiodate, chemical evidence was obtained which indicated an oxidation–reduction reaction between periodic acid and divalent cobalt as a function of the hydrogen ion concentration. This reaction does not appear to be clearly indicated in the literature. Gmelin's "Handbuch"<sup>3</sup> leaves the matter an open question in citing two papers with

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(3) "Gmelin's Handbuch der anorganischen Chemie," No. 58 Cobalt, Part A, Sect. 2, 8th ed., Verlag Chemie G.m.b.h., Berlin, 1932, p. 317.

(2) M. B. Epstein, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **48**, 379 (1949).

(3) V. I. Komarevsky and J. R. Coley, *THIS JOURNAL*, **70**, 4163 (1948).