metal oxide catalysts in vapor phase hydrogenation and dehydrogenation reactions. It is known that cycloölefins 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,[2] *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°, $n^{20}D$ 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.[1]

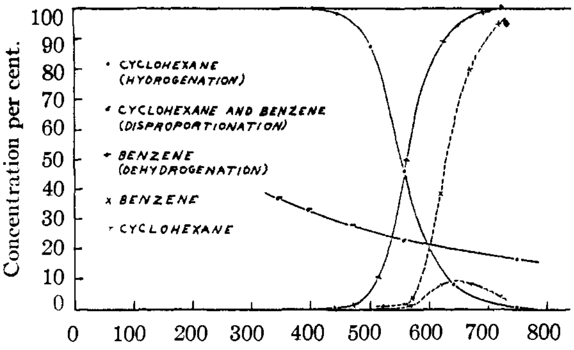

Fig. 1.—Reaction of cyclohexene and hydrogen. Theoretical equilibrium concentrations (solid lines) and experimental results (dotted line) over vanadia catalyst.

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[3] 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 indicates 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.	$n^{20}D$ of the product	Chromatographic analysis[a] of the product (%) C_6H_{10}	C_6H_6	C_6H_{12}
		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

[a] Initial boiling point of all products was 80° which clearly indicated that no isomerization to methylcyclopentane or methylcyclopentene took place.

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[2] M. B. Epstein, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **42**, 379 (1949).

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

The Reaction between Periodate and Cobaltous Ions[1]

BY RALPH E. JENTOFT AND REX J. ROBINSON[2]

RECEIVED MARCH 23, 1953

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"[3] leaves the matter an open question in citing two papers with

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[1] This work was partly supported by the Office of Naval Research under Contract No. N8onr-520/III with the University of Washington.

[2] Correspondence should be addressed to Rex J. Robinson.

[3] "Gmelins Handbuch der anorganischen Chemie," No. 58 Cobalt, Part A, Sect. 2, 8th ed., Verlag Chemie G.m.b.h., Berlin, 1932, p. 317.

opposing views. More recently other workers[4,5] have reported the existence of certain cobaltous periodates in complete variance with the present findings.

Some revealing information regarding this question is obtained through a consideration of oxidation potentials. In Fig. 1 are shown portions of the potential-*p*H diagram for iodine and cobalt concoustructed from the data of Latimer[6] as described by Delahay, Pourbaix and Van Rysselberghe.[7] (Although the potential of the periodate—iodate couple is based upon purely chemical evidence, it represents a close approximation). Thus it is seen that the stability of a strongly acid solution of cobaltous and periodate ions is indicated, whereas in weakly acid solution the reduction of periodate by the cobaltous ion appears possible.

The chemical evidence indicating this reaction was the production of gelatinous, greenish-brown cobaltic hydroxide and iodate ions when solutions of divalent cobalt and periodic acid were mixed. The cobaltic hydroxide was identified on the basis of its physical properties and the knowledge of the reactants and possible products. After filtration of the cobaltic hydroxide, iodate was identified in the filtrate with silver nitrate solution by the formation of white, curdy silver iodate, difficultly soluble in nitric acid (brown silver periodate is soluble). At a *p*H of about 2 this reaction proceeded very slowly, traces of the reaction products appearing after about 15 minutes. Many hours later the reaction was still far from complete as judged by the small amount of cobaltic hydroxide formed. In more acid solution the reaction did not go at all. However at *p*H 6 it was instantaneous even in dilute solutions.

Quantitative tests were performed to firmly establish the existence of this reaction. Cobaltous acetate solution in excess reacted with a known amount of potassium metaperiodate in solution. The oxidation state of the iodine after reaction was established iodometrically. Cobaltic ion in an acid solution is an oxidizing agent and would interfere in the iodometric procedure. Removal of the gelatinous cobaltic hydroxide was not practical so the cobalt was converted to the cobaltous state. This reduction occurred spontaneously when the cobaltic hydroxide was dissolved by heating in a 0.1 *N* sulfuric acid solution. A few drops of ethylenediamine were added to assist, through its complexing action with cobalt, in the solution of the difficultly soluble cobaltic hydroxide. Controls were run with identical treatments except that the solutions were acidified before mixing to prevent the reaction under study from occurring. The results are shown in Table I.

The ratio of the average number of oxidation equivalents found after reaction to the number of oxidation equivalents taken is 0.740 compared to the theoretical value of 0.750 if the equivalents of periodate were all reduced to iodate. The same ratio for the controls is 0.988 compared to the theoretical value of 1.000 if the periodate solution had not reacted.

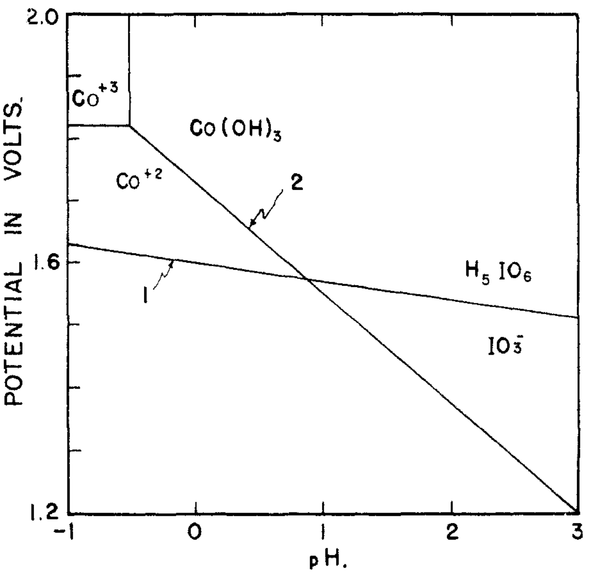

Fig. 1.—A portion of the potential-*p*H diagram for the $Co(OH)_3$–Co^{++} and the H_5IO_6–IO_3^- couples.

TABLE I

ANALYTICAL DATA FOR THE REACTION BETWEEN Co^{++} AND IO_4^-

	Oxidation equivalents	
Taken	Found after reaction	Found in controls
0.656	0.493	0.654
	.495	.650
	.474	.635
	.479	.652
	.484	
Av.	0.485	0.648

It is believed that the above facts clearly establish the existence of an oxidation–reduction reaction between periodate and divalent cobalt. The probable reaction is indicated by the equation.

$$2Co^{++} + IO_4^- + (n + 2)H_2O \longrightarrow Co_2O_3 \cdot nH_2O + IO_3^- + 4H^+$$

It is of interest to note that in agreement with the postulated formation of hydrogen ions here, a decrease in *p*H has been noted after the reaction of solutions originally at *p*H 6.

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Peptides Isolated from a Partial Hydrolysate of Steer Hide Collagen

BY THOMAS D. KRONER, WILLIAM TABROFF AND JOHN J. MCGARR

RECEIVED APRIL 18, 1953

In the work on the determination of the structure of collagen being performed in these laboratories, we have been concerned with the sequences of the amino acid residues in the polypeptide chains of

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[4] R. K. Bahl, S. Singh and N. K. Bali, *J. Indian Chem. Soc.*, **20**, 227 (1943).

[5] R. C. Sahney, S. L. Aggarwal and M. Singh, *ibid.*, **24**, 193 (1947).

[6] W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952, pp. 210–213.

[7] P. Delahay, M. Pourbaix and P. Van Rysselberghe, *J. Chem. Education*, **27**, 683 (1950).