

STUDIES ON THE CATALYTIC FORMATION OF DIOLEFINS FROM MONO-OLEFINS.

PART III. CATALYTIC DEHYDROGENATION OF BUTENE IN THE PRESENCE OF AIR AT REDUCED PRESSURES.

By A. N. ROY, *Department of Pure and Applied Chemistry, Indian Institute of Science, Bangalore.*

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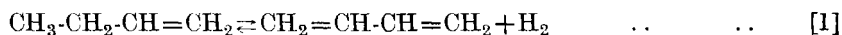
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ABSTRACT.

Catalytic dehydrogenation of butene in the presence of air has been studied at reduced pressures. Preliminary experiments performed with varied proportions of butene and air over $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$ catalyst at 15–30 mm. of Hg. and 440–500°C. indicated interaction of the hydrogen, formed through dissociation of butene, with oxygen of the air to a limited extent with slight increase in the yield of butadiene. Use of ratio of air to butene greater than 1 : 1 was detrimental to the reaction. Quantitative study of the velocity of reaction was carried out at 520–600°C. and 160–230 mm. of Hg. From a comparison of the experimental values for the degree of dissociation of butene with the theoretical values, it was found that equilibrium in butene-air system was not attained. However as a result of the interaction of oxygen with hydrogen produced by dissociation, it has been possible to secure yield of butadiene-1,3 up to 34.9% at 550°C. and 165 mm. of Hg.

Studies on the dehydrogenation of butene over various catalysts and under different operating conditions revealed to a great extent the limitations under which the reaction has to be carried out. In this reaction, besides the specificity of the catalyst, consideration of temperature and pressure are of particular importance. For example, at atmospheric pressure, the primary dehydrogenation of butene proceeds only to a limited extent and the yield of butadiene does not exceed 14% at 560°C. The reaction temperature cannot be increased above this limit due to the occurrence of secondary reactions. Experiments carried out at the low pressures of 10–50 mm. and between 440° and 500°C. gave butadiene in yields which corresponded with equilibrium conditions but such low pressure reactions, excepting for their theoretical importance, are not of much practical value. In view of the great technical value of this reaction, it was felt necessary to investigate the possible methods of effecting an equilibrium shift of the reaction, favourable to the formation of butadiene, at total pressures which are industrially workable.

The essential condition in causing a shift of the reaction



to the right involves removal of hydrogen obtained as reaction product simultaneously with its formation on the catalyst surface. This may be done by selective interaction of hydrogen with molecules like oxygen, carbon monoxide, carbon dioxide and certain unsaturated hydrocarbons such as acetylene, ethylene, etc.

The possibility of employing air for selective oxidation of hydrogen, formed in the dehydrogenation reactions with beneficial effects, can be seen from the work of Forlich and Wiezevich (1935). They dehydrogenated propane by using 70% air in a copper reactor at 600°C. and obtained a conversion of 75–80% unsaturated hydrocarbons consisting of propylene and ethylene. Further, it is also known that hydrogen can be removed from gases rich in olefins by selective oxidation with air or oxygen in the presence of a catalyst such as copper oxide with practically no simultaneous loss of hydrocarbon constituents (1934). Therefore, it seemed possible to effect the simultaneous dehydrogenation of butene to butadiene and oxidation of hydrogen with air provided a suitable catalyst is found. And such a catalyst can be expected among the complex 'oxide-metal' type. A few experiments have therefore been carried out with mixtures of butene and air using different types of catalysts. Of the several catalysts

tried, the one composed of Cr_2O_3 (80%)- Al_2O_3 (5%)-Cu (15%) has been found to be most efficient. Quantitative measurements of the velocities of the simultaneous reactions (1) and (2) over this catalyst have been carried out at the pressures of 160–230 mm. and 520–600°C., to determine the effect of air in increasing the degrees of dissociation of butene, and how far these values compare with the theoretical values, if equilibrium could have been attained.

EXPERIMENTAL.

Material: Butene was prepared by the dehydration of *n*-butyl alcohol over activated alumina at 400°C.

Catalyst: Chromium oxide-alumina (5%) promoted by 15% copper was dried at 550°C. and 0.5–0.2 mm. of mercury and used in all the experiments. The method of its preparation is given in Part I.

Apparatus and Procedure: The arrangement of the apparatus for the present investigation was essentially the same as given in Fig. 1 (Part I). For the purpose of controlling pressures in the range of 160–230 mm. in the system, a capillary leak-control was provided in the bottle *B*. The gas-holder *A*, was filled with a mixture of butene and air (ratio 1 : 1). Before starting an experiment the system was evacuated and the catalyst was heated to the desired temperature. After this, the butene-air mixture from the gas-holder *A*, was released through V_1 into the reaction chamber with simultaneous regulation of the capillary leak in *B*, so that a steady rate of flow of the gas at a desired pressure was maintained in the system. Under this regulated condition, the reaction was allowed to proceed for some time after which the actual observations were taken. As usual, the gaseous reaction products were collected in the liquid air trap T_2 and analysed for butene, butadiene-1,3 and water.

Water: Water collected in the trap T_2 was found contaminated with hydrocarbons and therefore could not be estimated by any direct method. An indirect method involving estimation of acetylene formed by the action of water on calcium carbide according to the equation :—



Results: The yields of butadiene-1,3 obtained on dehydrogenation of butene mixed with air, over Cr_2O_3 - Al_2O_3 -Cu catalyst at 440–500°C. and 15–30 mm. of mercury are given in Table I.

TABLE I.

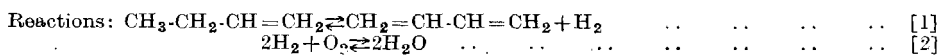
No.	Temp. °C.	Pressure in mm.	Ratio of Air: Butene.	Yield of butadiene, %.
1	440	18	50 : 50	30.0
2	440	15	50 : 50	30.2
3	470	28	54 : 46	38.2
4	470	27	34 ; 66	41.3
5	500	30	39 : 61	47.4
6	500	30	50 : 50	46.5
7	500	30	66 : 34	37.8
8	500	30	70 : 30	31.6

On comparing the above result with those obtained with pure butene over the same catalyst (*vide* Part I, Tables V, VI, VII) it will be seen that an increase of 4.8% in the yield of butadiene has been secured at 500°C. and 30 mm. pressure by using about 40% air. This increase in the yield of butadiene may be due to two causes: (i) occurrence of the reaction [2], and (ii) lowering of the partial pressure of butene by air. That the reaction [2] had taken place was confirmed by observing formation of water along with butadiene. The last four experiments indicate that use of more than an equivalent volume of air is detrimental to the formation of butadiene. From these experiments it is not however clear whether the use of air had any beneficial effect on the dehydrogenation reaction as a whole because the extent of increase in the degree of dissociation, considering the lowering of partial pressure of butene, is small.

It was hoped that simultaneous dehydrogenation and removal of hydrogen from butene with air in the ratio 1 : 1 over Cr_2O_3 - Al_2O_3 -Cu catalyst at 160–230 mm. and between 500–550°C.

might result in yield of butadiene which would have technical significance. These are conditions where, as shown in Part I, dehydrogenation of pure butene does not attain equilibrium. Data for some typical experiments are given in Table II. From the data given in Table II, we have calculated the exact volumes of butadiene, butene, water vapour and the remaining gas (Table III), that contributed to the total pressure of the reaction for the experiments performed at 520°C. and 550°C. Experiments made at 600°C. were vitiated through the occurrence of secondary reactions and therefore have not been included in the table.

TABLE II.



Catalyst: Cr₂O₃ (80%)-Al₂O₃ (5%)-Cu (15%)

Butene to air = 1 : 1; Duration of each expt. is approximately one hour.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp. 10	Exp. 11	Exp. 12
1. Temperature, °C. ..	520	520	520	520	520	550	550	550	550	550	600	600
2. Pressure in mm. of Hg ..	160	190	200	225	230	160	165	200	225	225	165	225
3. Total vol. of gas passed, c.c.	560	500	615	550	590	630	710	790	750	685	650	760
4. Vol. of butene-butadiene, collected, c.c. ..	245	230	282	245	267	286	295	344	332	305	276	306
5. Space velocity * ..	51.6	39.3	49.2	44.7	47.2	50.3	56.8	62.9	59.6	53.8	51.5	60.7
6. Yield of butadiene, % on the total vol. of butene-butadiene collected ..	25.1	23.5	22.4	24.0	17.9	33.5	34.9	27.9	29.0	31.6	32.0	28.2
7. Vol. of acetylene formed, c.c.	14.6	12.0	14.1	12.6	10.6	27.6	31.0	26.8	25.0	23.6	19.2	15.3
8. Loss of butene on the vol. passed, % ..	12.5	8.0	8.3	10.9	9.4	9.3	16.8	12.7	11.5	10.9	15.1	19.2

* Volume of the gas at N.T.P. passed per c.c. of the catalyst per hour.

TABLE III.

Experiment Nos.	1	2	3	4	5	6	7	8	9	10
1. Vol. of butene, c.c. ..	183.5	176	218.8	186.2	219.4	190.2	191.9	248.1	235.7	208.6
2. Vol. of butadiene, c.c. ..	61.5	54.0	63.2	58.8	47.6	95.8	103.1	95.9	96.3	96.4
3. Vol. of water vapour corresponding to the vol. of C ₂ H ₂ formed, c.c. ..	29.2	24.0	28.2	25.2	21.2	55.2	62.0	53.6	50.0	47.2
4. Vol. of remaining gases, c.c. ..	297.9	268.0	328.4	296.0	310.8	328.0	365.1	410.5	396.3	368.1
5. Total vol. of the gases, c.c. ..	572.1	522.0	638.6	566.2	599.0	669.2	722.1	808.1	778.3	720.3

Assuming that no hydrogen has been removed by combination with oxygen, which is not actually the case as shown in horizontal column 3 (Table IV), the minimum partial pressure of butadiene in the system if equilibrium were established could be calculated from extrapolated values of K_p at these higher temperatures from the equation,

$$K_p = \frac{P_{\text{Butadiene}} \times P_{\text{H}_2}}{P_{\text{Butene}}} = \frac{[P_{\text{Butadiene}}]^2}{P_{\text{Butene}}}$$

The extrapolated value of K_p at 520° is 0.015 and at 550° is 0.03. The degree of dissociation of butene calculated on the basis of this minimum value of partial pressure of butadiene, are given in Table IV as α , calculated from K_p .

TABLE IV.

Experiment No.	PC_4H_8	PC_4H_6	P_{H_2} (corresp. to butadiene).	Total P due to the reacting system.	Experimental value of α .	Calculated value of α from Kp .	P_{H_2O}	Temp. °C.
1	51.3	17.2	17.2	85.7	0.25	0.34	8.2	520
2	64.1	19.7	19.7	103.5	0.23	0.31	8.7	520
3	68.5	19.8	19.8	108.1	0.22	0.30	8.8	520
4	74.0	23.4	23.4	120.8	0.24	0.29	10.0	520
5	84.2	18.3	18.3	120.8	0.17	0.29	8.2	520
6	45.5	22.9	22.9	91.3	0.33	0.44	13.2	550
7	43.8	23.6	23.6	91.0	0.35	0.44	14.2	550
8	61.4	23.7	23.7	108.8	0.27	0.40	13.3	550
9	68.1	27.9	27.9	123.9	0.29	0.39	14.5	550
10	65.2	30.1	30.1	125.4	0.31	0.36	14.7	550

On comparing the experimental values for α with the theoretical values even on the assumption that no hydrogen has been removed by oxidation, a marked difference is observed. This indicates that reaction [1] did not attain equilibrium in butene-air system. However, the beneficial effect of air in the dehydrogenation reaction will be apparent if we compare the present results with those obtained by Grosse, Morrell and Mavity (1940) on the dehydrogenation of butene to butadiene-1,3 over chromium oxide-alumina catalyst at reduced pressure, viz. 0.25 atmosphere and 600–650°C. A portion of their data is reproduced below:

Dehydrogenation of Butene.

Experiment No.	Temp. °C.	Pressure in mm.	Contact time sec.	Yield of butadiene single pass, %.	Carbon wt. percentage of charge.
2	600	190	0.70	22.0	11.2
4	600	168	0.34	21.4	4.8
5	600	197	0.12	13.4	1.5

From the data of Grosse *et al*, it will be seen that they obtained only 21.4% yield of butadiene at 600°C. and 168 mm. pressure and therefore the present yield of 35% butadiene at 550°C. and a total pressure of 160 mm. is of considerable technical significance [Experiment 7]. This improved yield of butadiene in butene-air system is evidently due to a shift of the reaction [1] through the occurrence of the reaction [2]. The extent of interaction of hydrogen produced by dissociation of butene with oxygen of the air, may be seen from the partial pressures of water vapour given in Table IV.

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