

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

PART I. CHEMICAL EQUILIBRIUM IN BUTADIENE-1,3 FORMATION FROM BUTENE-1 AT LOW PRESSURES.

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ABSTRACT.

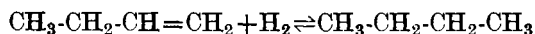
In view of the difficulties involved in the determination of chemical equilibrium in the dehydrogenation of butene-1 to butadiene-1,3 at atmospheric pressure, an apparatus has been specially devised to study the reaction at the low pressures of 10–50 mm. and in the temperature range of 360–520°C. The reaction has been studied in detail over the following three catalysts: (1) $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, (2) $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-Mo}_2\text{O}_3$, (3) $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$, of which the catalyst No. (3) promoted by copper has been found most efficient. The equilibrium constants of the reaction have been determined at five temperatures. From the values of the equilibrium constant, the heat of reaction, the free energy and the temperature of neutral equilibrium have been calculated.

The difficulties involved in the selective initiation of the dehydrogenation of butene-1 to butadiene-1,3 at atmospheric pressure



were apparent from our preliminary study of the reaction over a variety of dehydrogenation catalysts. Even in the presence of a highly specific catalyst such as $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5%), the reaction rate was very slow and the degree of dissociation did not exceed 0.14 at 560°C. Above this temperature the primary process of dehydrogenation was complicated by the secondary reactions involving polymerisation, aromatisation and decomposition. Dement'va and his collaborators (1937) attempted to study the equilibrium at atmospheric pressure and obtained values for the equilibrium constant varying from 0.0019 to 0.0058 at 480°C. and 0.005 to 0.025 at 540°C. The factors which influence the equilibrium are:—

1. Increase in temperature increases dissociation, i.e. equilibrium shifts to the diolefin side.
2. Lowering of pressure favours dehydrogenation since the reaction to the diolefin side represents an increase in the number of molecules.
3. Butene in the presence of hydrogen is also in equilibrium with the paraffin hydrocarbon.



Reaction (3), however, need not be taken into account since it is negligible under the present conditions. These considerations indicate the necessity of performing the reaction at considerably lower pressures and in the presence of a stable and highly specific dehydrogenating catalyst for the accurate determination of the equilibrium constant.

Catalyst: The essential requirement in the present study consisted in the finding out of a proper catalyst which should permit the reaction to attain equilibrium at low pressures and at comparatively low temperatures. Of the large body of oxide catalysts known for their efficiency of dehydrogenation, the most important are, Cr_2O_3 , Mo_2O_3 , V_2O_5 , ZnO_2 , etc. In addition to these, certain metals such as Fe, Ni, Co, Cu and platinum are also very efficient in many hydrogenation-dehydrogenation reactions.

Dehydrogenation of butene-1, over chromium oxide gel stabilised by 5% Al_2O_3 has been studied in detail. This catalyst, in spite of its high specificity and stability, did not permit dissociation of butene to reach equilibrium in the temperature range of 360–520°C. and at pressures of 10–50 mm. Addition of small amounts of the oxides of vanadium and molybdenum is claimed (Balandin and Brussow, 1936; Taylor and Yeddanapalli, 1938) to promote the activity of chromium oxide catalyst. A catalyst consisting of Cr_2O_3 (80%), Al_2O_3 (5%),

Mo_2O_3 (2.5%), and V_2O_3 (2.5%) was therefore prepared and studied. Its activity was more or less the same as that of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5%). Of the two metals, nickel and copper, which function as promoters to hydrogenating and dehydrogenating catalysts, the use of nickel is limited because of its known tendency to break C-C bonds with formation of metallic carbides and lower hydrocarbon fission products. This has actually been observed in the present investigation. Incorporation of 5% nickel to $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, resulted in vigorous decomposition of butene even in the neighbourhood of 450°C. Metallic copper, however, manifests a marked inertness to fission of the C-C bond but suffers from the well-known disadvantage that in the neighbourhood of 400°C. it suffers rapid deterioration in activity due to the process of sintering. However, the use of copper as a promoter of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ can be expected if it is properly stabilised and such a catalyst would increase the reaction rate at comparatively lower temperatures, since it is characteristic of the metals to exercise their activity in a lower temperature range than is required by the oxide catalysts. This has been found to be the case. The catalyst consists of Cr_2O_3 (85%), Al_2O_3 (5%) and Cu (10%). This catalyst showed remarkable activity and up to the temperature of 500°C. there was practically no deterioration. Another catalyst of this composition was prepared by simple incorporation of CuO to $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ gel with subsequent reduction at 300°C.; the dehydrogenation activity was practically the same as that of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst, but the activity fell with increase in the reaction temperature.

Experiments have been carried out in a flow system, specially devised for the study of the reaction at pressures of 10–50 mm. and in the temperature range of 360–520°C. Of the many catalysts tried, the following three (1) $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5%), (2) $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5%)- Mo_2O_3 (2.5%)- V_2O_3 (2.5%), (3) $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5%)-Cu (10%), have been employed for the detailed study of the reaction and the results are given in the experimental part.

EXPERIMENTAL.

Materials: Butene-1, was obtained by the dehydration of *n*-butyl alcohol (B.P. 114-114.5/684 mm.) over activated alumina (Ipatief, Pines and Schead, 1934). The gas was then purified by bubbling through two wash bottles, the first one containing 50% sulphuric acid and the second one 50% potassium hydroxide solution. For the final purification of butene, it was liquefied and carefully fractionated and only the middle fraction was employed for the equilibrium study. The purity of the gas was determined by absorption over 87% sulphuric acid.

Catalyst:

(1) *Chromium oxide-alumina:* $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5%). To a mixed solution of chromium nitrate and aluminium nitrate (approx. strength 0.2N), dilute ammonia was slowly added with constant stirring till it was just basic to litmus paper. On heating on a water bath for about 2 hours, the precipitation of the hydroxide gel was complete. The gel was then filtered under suction, washed with distilled water, dried at 100–150°C. and finally heated at 575°C. for 6-7 hours in a current of hydrogen.

(2) *Chromium oxide-alumina-vanadium oxide-molybdenum oxide:* Cr_2O_3 -(90%)- Al_2O_3 (5%)- V_2O_3 (2.5%)- Mo_2O_3 (2.5%). Calculated quantities of ammonium metavanadate and ammonium molybdate were thoroughly mixed with a freshly precipitated mixed hydroxide gel of chromium and aluminium. The mass was then dried on a water bath and subsequently heated in a current of hydrogen at 450–500°C. for a period of about 12 hours.

(3) *Chromium oxide-alumina-copper:* Cr_2O_3 (85%)- Al_2O_3 -(5%)-Cu (10%). To a freshly prepared mixed hydroxide gel of chromium and aluminium free from electrolytes, was added a solution of copper formate in calculated amount so as to obtain a mixed catalyst of the following composition: Cr_2O_3 —85%, Al_2O_3 —5%, Cu—10%. This mass was then dried on a water bath and slowly heated at 100–150°C. in an air oven. It was then broken into pieces, sieved to obtain granules (15–20 mesh) and reduced in a current of hydrogen at 250–300°C. for a period of 12 hours.

Apparatus and Procedure: Experimental arrangement of the apparatus is diagrammatically explained in Fig. 1.

The apparatus was essentially constructed to carry out experiments at the low pressures of 10–50 mm. and in the temperature range of 360–540°C. Butene-1, kept in the large glass carboy *A* (50 litres capacity), maintained slightly above the atmospheric pressure by the levelling bulb *L*, was drawn through the fine capillary *C* into the reaction tube *R*, by the high vacuum Cenco pump *P*. Two valves V_1 and V_2 were used to regulate the rate of flow and pressure

drop of butene in the reaction chamber. The bottle B_1 of about 2.5 litres capacity was provided in the system for ensuring the maintenance of constant pressure for long periods. The rate of flow of butene was measured by the carefully calibrated flow-meter F and the reaction pressure read by the mercury manometer M . The U-tubes U_1 and U_2 containing anhydrous calcium chloride served to dry the gas. The reaction tube R was heated in the electric furnace H , the temperature of which was carefully controlled. For collecting the products of reaction the traps T_1 and T_2 were used. T_1 served to collect any high boiling polymer that might be formed in the reaction and T_2 , immersed in liquid air contained in the Dewar's flask D collected all other gaseous products except hydrogen. The two towers W_1 and W_2 contained sodalime-calcium chloride and potassium hydroxide respectively. B_1 is simply a safety bottle for the oil pump.

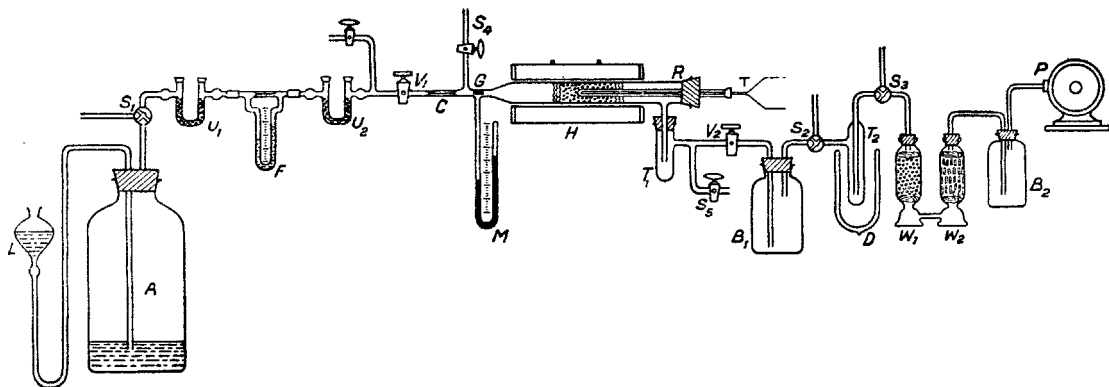


FIG. 1.

Before starting an experiment, the valve V_1 was closed to A , the pump P was worked, and the system was thoroughly evacuated. A piece of reduced copper gauze G inserted in between M and R , served to catch any trace of mercury vapour that might be carried into R during high evacuation. The reaction tube containing catalyst was then heated to a constant temperature which was measured by the thermocouple T imbedded in the catalyst. Butene-1, from the gas holder A was next allowed to enter the reaction chamber by opening the valve V_1 and the desired rate of flow and the reaction pressure were secured by carefully regulating V_1 and V_2 and the length of the capillary C . Before taking any observation the apparatus was run for a considerable time to ensure steady conditions of equilibrium. The reaction product, consisting of butene and butadiene was collected in the liquid air trap T_2 for about an hour. After the experiment, T_2 was isolated from the rest of the apparatus by means of the two 3-way stop-cocks S_2 and S_3 , and the reaction product, taken out through S_2 , was analysed for butadiene and butene.

Analysis: Butadiene-1,3 was analysed by absorption in molten maleic anhydride and the apparatus used for this purpose was essentially the same as that of Shu Kambara (1939). Butene-1 was analysed by absorption in 87% sulphuric acid.

Tables I and II refer to the values of the degrees of dissociation as obtained over $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Mo}_2\text{O}_3\text{-V}_2\text{O}_5$ catalysts respectively. The last five tables, namely, III, IV, V, VI and VII give data for the equilibrium constants obtained by the use of the most effective $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$ catalyst. In all the experiments, the volume of the catalyst was about 10 c.c. and free space 60%. The rate of flow of butene was varied between 150 to 400 c.c. per hour. In the course of this study three fresh preparations of the catalysts No. 1 and No. 3 were employed with satisfactory uniformity in their activities. The equilibrium constants have been calculated from the equation.

$$K_p = \left[\frac{a^2}{1-a^2} \right] \frac{p}{760}$$

where a is the degree of dissociation of a gram mole of butene and p is the reaction pressure in mm. of mercury.

Dehydrogenation of Butene-1 over Cr₂O₃-Al₂O₃ (5%) catalyst.

TABLE I.

No.	Temp. °C.	The range of pressure studied in mm.	Variation of the degree of dissociation.
1	380	15-50	0.098-0.045
2	420	12-48	0.180-0.090
3	450	15-45	0.250-0.141
4	480	15-50	0.412-0.245
5	520	18-45	0.502-0.336

Dehydrogenation of Butene-1 over Cr₂O₃-Al₂O₃ (5%)-Mo₂O₃ (2.5%)-V₂O₃ (2.5%).

TABLE II.

No.	Temp. °C.	The range of pressure studied in mm.	Variation of the degree of dissociation.
1	400	15-35	0.151-0.093
2	440	12-25	0.268-0.200
3	470	15-33	0.364-0.228
4	500	15-36	0.465-0.330

Dehydrogenation Equilibrium of Butene-1, over Cr₂O₃ (85%)-Al₂O₃ (5%)-Cu (10%) catalyst.

TABLE III.

Conditions: Temperature = 370°C. Rate of flow = 150-300 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{a^2p}{1-a^2}$
1	12	0.126	0.193
2	12	0.120	0.175
3	18	0.102	0.189
4	18	0.098	0.174
5	25	0.091	0.207
6	35	0.070	0.172

Average value = 0.185

 $K_p = 0.000,24.$

TABLE IV.

Conditions: Temperature = 410°C. Rate of flow = 150-300 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{a^2p}{1-a^2}$
1	15	0.200	0.624
2	15	0.202	0.637
3	18	0.183	0.623
4	18	0.180	0.601
5	27	0.154	0.656

Average value = 0.628

 $K_p = 0.000,82.$

TABLE V.

Conditions: Temperature = 440°C. Rate of flow = 150-350 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{a^2p}{1-a^2}$
1	12	0.330	1.47
2	12	0.334	1.51
3	16	0.300	1.58
4	22	0.251	1.48
5	27	0.240	1.65
6	35	0.219	1.76

Average value = 1.58
 $Kp = 0.002,08$

TABLE VI.

Conditions: Temperature = 470°C. Rate of flow = 200-400 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{a^2p}{1-a^2}$
1	18	0.396	3.34
2	18	0.400	3.42
3	23	0.380	3.88
4	24	0.368	3.75
5	35	0.300	3.46

Average value = 3.57
 $Kp = 0.004,70.$

TABLE VII.

Conditions: Temperature = 500°C. Rate of flow = 200-500 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{a^2p}{1-a^2}$
1	12	0.550	5.21
2	15	0.530	5.86
3	18	0.516	6.53
4	22	0.480	6.58
5	30	0.426	6.64
6	35	0.380	5.80

Average value = 6.58
 (Nos. 3, 4 and 5)
 $Kp = 0.008,66.$

Heat of Reaction: It will be seen from the accompanying tables that consistent and reliable data for the equilibrium constant Kp are obtained with chromic oxide-alumina-copper catalyst. With the other catalysts, somewhat lower values for the degrees dissociation have been obtained. The relation between the heat of reaction, ΔH_T and the equilibrium constant Kp is given by the relation:

$$\frac{\partial \ln Kp}{\partial T} = \frac{\Delta H}{RT^2} \quad \dots \quad (1)$$

If it is assumed that ΔH_T is independent of temperature between T_1 and T_2 ($T_2 > T_1$), the expression (1) may be integrated as follows:—

$$\Delta H = R (\ln K_2 - \ln K_1) \frac{T_1 T_2}{T_2 - T_1} \quad \dots \quad (2)$$

Instead of calculating ΔH_T from (2), graphical method is usually used, since it gives more satisfactory results. The value of ΔH_T for butene \rightleftharpoons butadiene as obtained from equilibrium data by the graphical method is: $\Delta H_T = 28,600$ cal. (Temperature range 370–500°C.)

It should be noted here that the above value of ΔH_T is only an approximate estimation. The standard value of ΔH_T for the reaction is given in a subsequent paper.

Free Energy of Reaction: From the values of the equilibrium constant (Tables III to VII), the free energies at five different temperatures have been calculated by using the well-known equation $\Delta F_T = -RT \ln K_p$. The values of ΔF_T and the corresponding reaction temperatures are given in Table VIII:

TABLE VIII.

No.	Temp. °C.	Temp. °K.	K_p .	ΔF_T ; cal.
1	370	643	0.000,24	10,620
2	410	683	0.000,82	9,642
3	440	713	0.002,08	8,748
4	470	743	0.004,70	7,911
5	500	773	0.008,66	7,294

ΔF_T as a linear function of temperature, can be expressed in the form of $\Delta F_T = A + BT$.

Thus using, $\Delta F_T = 9,642$ at 683°K .

$\Delta F_T = 7,911$ at 743°K .

we have, $\Delta F_T = 29,352 - 28.85T$.

From the above equation, the temperature of neutral equilibrium, i.e. temperature at which $\Delta F_T = 0$, is: $T_0 = 744^\circ\text{C}$.

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