

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

## PART IV. STUDIES ON CHEMICAL EQUILIBRIUM IN ISOPRENE FORMATION FROM 3-METHYL-BUTENE-1 AT LOW PRESSURES.

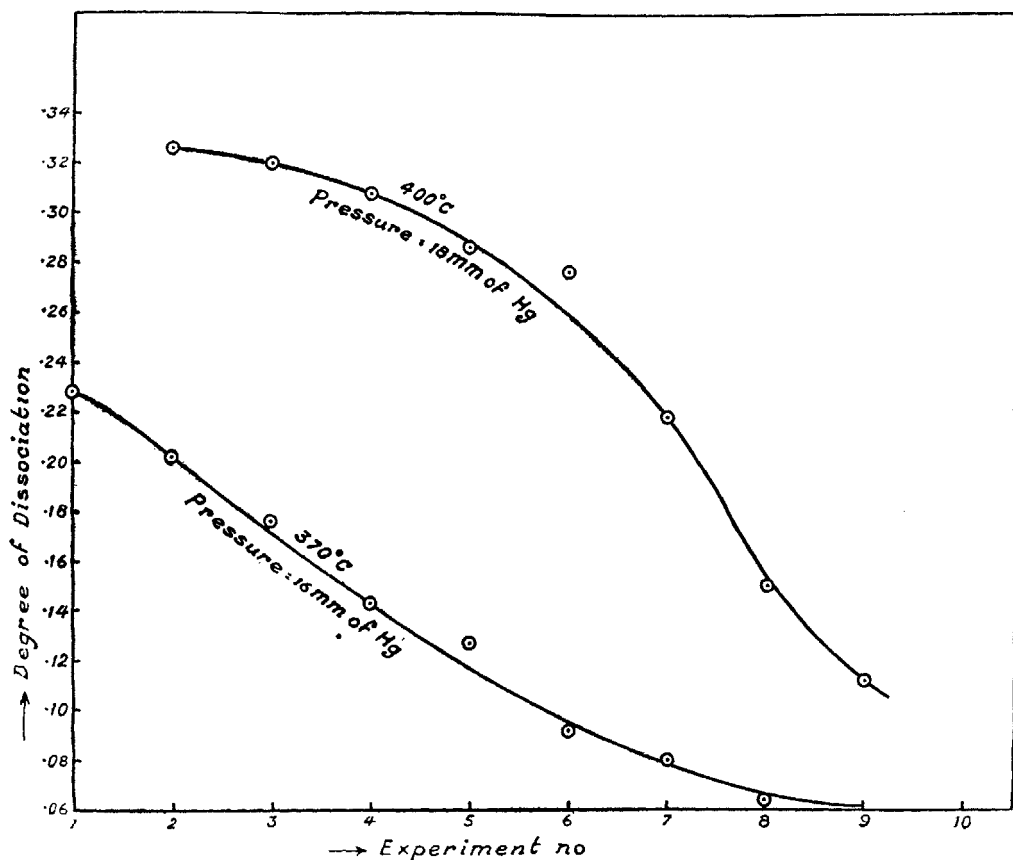
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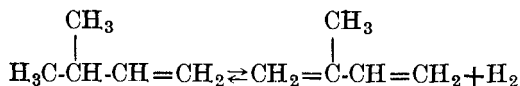
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### SUMMARY.

Chemical equilibrium in the dehydrogenation of 3-methyl-butene-1 to isoprene has been studied at the low pressures of 10-35 mm. and at 330-450°C., over  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-Mo}_2\text{O}_3$  catalyst. The activity of the catalyst was maintained steady by periodic activation in a current of hydrogen at 575°C. From the values of the equilibrium constant, determined at four different temperatures, the heat of reaction, the free energy of reaction and the temperature of neutral equilibrium have been calculated.

In a previous paper (Part I) a detailed description has been given of the study of the equilibrium of dehydrogenation of butene-1 to butadiene-1,3 carried out at the low pressures of 10-50 mm. and in the temperature range of 360-500°C. This experimental technique has now been extended to the study of the equilibrium in the dehydrogenation of the branched chain olefin 3-methyl-butene-1 to the corresponding diolefin isoprene (3-methyl-butadiene-1,3).





The essential requirement in the present study consisted in first finding out a suitable catalyst and proper operating conditions which would permit the dehydrogenation reaction to attain equilibrium with sufficiently rapid speed. The three catalysts, namely, (1)  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ , (2)  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-Mo}_2\text{O}_3$ , and (3)  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$ , whose efficiencies have already been studied in connection with butene-1-butadiene-1,3 equilibrium have been tried. In course of this trial it was observed that these catalysts were initially very active and permitted high degrees of dissociation of 3-methyl-butene-1 to isoprene at 330–450°C. and 12–35 mm. of mercury, but it was extremely difficult to maintain this activity which progressively decreased with the length of pass.

In order to find out the causes which led to this poisoning a large number of catalyst samples were prepared under controlled conditions and tested. As a typical case, the results obtained with  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  (5%)  $\text{-Mo}_2\text{O}_3$  (2.5%)  $\text{-V}_2\text{O}_5$  (2.5%) catalyst at 350°C. and 400°C. are shown in the accompanying graph (which represents the decrease in the degree of dissociation of 3-methyl-butene-1 in the successive experiments performed at regular intervals of time). It will be seen from the graph that the degree of dissociation of 3-methyl-butene-1 progressively decreased in the successive experiments which was gradual and slow in the first few experiments but rapid afterwards. Further, this was more pronounced at the lower temperature of 350°C. Experiments were next carried out to reactivate the catalyst. It was found that the catalyst on treatment with hydrogen at 575–600°C. for about 3–4 hours completely recovered its original activity (*vide* Part II). This clearly proved the deactivation was due to a temporary saturation of the active parts of the catalyst by the unsaturated hydrocarbon. Of the three catalysts tried, the activities of a specially prepared  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Mo}_2\text{O}_3\text{-V}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$  were practically the same but that of  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  was slightly lower. For the present work,  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Mo}_2\text{O}_3\text{-V}_2\text{O}_5$  catalyst has been found more suitable than  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$  catalyst, since its periodic regeneration in the course of the investigation was easier as it could be subjected to a hydrogen treatment at the elevated temperatures of 550–600°C.

#### EXPERIMENTAL.

*Material:* For the preparation of 3-methyl-butene-1 primary iso-amyl alcohol was dehydrated over Brockman's activated alumina at 400°C. The gaseous olefins thus obtained consisted of 93% 3-methyl-butene-1 and 7% of other isomers. In order to separate 3-methyl-butene-1 in a pure state, the product was subjected to a careful fractional distillation in a specially devised column and the fraction boiling at 16–17°C./684 mm. was used.

*Catalysts:* Preparation of the catalysts, (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%)  $\text{-Mo}_2\text{O}_3$  (2.5%)  $\text{-V}_2\text{O}_5$  (2.5%), and (3)  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cu}$  (10%), are given in detail in Part I. The catalyst No. (2), composed of the oxides of chromium, aluminium, vanadium and molybdenum, has been, however, prepared by the following modified method and used for the study of equilibrium of the reaction.

Chromium acetate (50 gms.) was slowly decomposed with dilute nitric acid and evaporated on a water bath until dry. The nitrate thus obtained was mixed with aluminium nitrate (5 gms.) and dissolved in 1.5 litres of water. The colloidal gel of the mixed hydroxides, obtained by addition of dilute ammonia in the usual way, was made ion free by hot water dialysis. The dialysed gel on drying on a water bath resulted in a powdery mass which was then intimately mixed with hot solutions of ammonium vanadate (2 gms.) and ammonium molybdate (2 gms.) to a thick paste. The paste was next allowed to set and dried at 150°C. To obtain the catalyst in granules of 15–20 mesh, the mass was carefully ground, sieved and reduced in a dry current of hydrogen at 575°C. for about 8 hours.

*Apparatus and Procedure:* The apparatus employed was essentially the same as given in Fig. 1 (Part I). Instead of the gas-holder A, a gas condensing trap of about 150 c.c. capacity containing liquefied 3-methyl-butene-1 and maintained at 0°C. by surrounding with ice in a Dewars cylinder, was attached to the system. Experiments were carried out in the temperature range of 330–450°C. and 12–35 mm. of mercury, by the procedure detailed in Part I. For the periodic activation of the catalyst the reaction tube was isolated from the rest of the apparatus by closing the valves  $V_1$  and  $V_2$ , and through the stop-cocks  $S_3$  and  $S_4$ , a current of hydrogen

was now allowed to pass over the catalyst heated at 550–575°C. for a period of 6–8 hours when complete restoration of the original activity of the catalyst took place.

*Analysis:* The reaction gas consisting of isoprene (B.P. 32-33/680 mm.) and 3-methyl-butene-1 (B.P. 16-17/680 mm.) partially condensed at the room temperature (28–30°C.). To avoid this difficulty sufficient nitrogen was mixed to keep them in vapour phase. Isoprene was then estimated by absorption in molten maleic anhydride and 3-methyl-butene-1, by absorption over concentrated sulphuric acid (90%).

*Results:* The equilibrium in the dehydrogenation of 3-methyl-butene-1 to isoprene (3-methyl-butadiene-1,3) has been studied over  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-Mo}_2\text{O}_7$  catalyst at 330–450°C. and 12–35 mm. of mercury. The results are given in Tables I, II, III and IV.

TABLE I.

Conditions: Temperature = 330°C. Rate of flow = 100–250 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{\alpha^2 p}{1-\alpha^2}$
1	12	0.125	0.193
2	12	0.132	0.213
3	12	0.140	0.240
4	17	0.110	0.208
5	17	0.980	0.165
6	18	0.100	0.200
7	25	0.082	0.170
8	27	0.086	0.201

Average value = 0.198  
 $K_p = 0.000,26$ .

TABLE II.

Conditions: Temperature = 370°C. Rate of flow = 100–300 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{\alpha^2 p}{1-\alpha^2}$
1	12	0.260	0.870
2	12	0.251	0.807
3	12	0.250	0.800
4	17	0.200	0.708
5	18	0.210	0.830
6	17	0.206	0.753
7	25	0.168	0.726
8	27	0.160	0.709
9	35	0.146	0.769
10	35	0.145	0.760

Average value = 0.773  
 $K_p = 0.001,02$ .

TABLE III.

Conditions: Temperature = 410°C. Rate of flow = 100–300 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{\alpha^2 p}{1-\alpha^2}$
1	15	0.400	2.86
2	15	0.410	3.03
3	16	0.398	3.04
4	25	0.310	2.65
5	25	0.315	2.75
6	27	0.300	2.67
7	34	0.282	2.90
8	34	0.280	2.89

Average value = 2.85  
 $K_p = 0.003,7$ .

TABLE IV.

Conditions: Temperature = 450°C. Rate of flow = 150-300 c.c. per hr.

No.	Pressure in mm.	Degree of dissociation.	$\frac{\alpha^2 p}{1-\alpha^2}$
1	17	0.600	9.56
2	17	0.585	8.84
3	17	0.590	9.07
4	26	0.500	8.66
5	26	0.485	7.99
6	28	0.480	8.38
7	35	0.430	7.94
8	35	0.420	7.49
9	37	0.420	7.92

Average value = 8.43  
 $K_p = 0.01, 1.$

*Heat of reaction*: The following value of the heat of reaction is obtained from the equilibrium data:

$$\Delta H_T = 27,120 \text{ calories. (Temperature range: 330-450°C.)}$$

*Free Energy of Reaction*: From the values of the equilibrium constant (Tables I-IV), the free energies at four different temperatures of reaction have been calculated by using the well-known relation  $\Delta F_T = -RT \ln K_p$ . The values of  $\Delta F_T$  are given in Table V.

TABLE V.

No.	Temp. °C.	Temperature (absolute).	$K_p$	$\Delta F_T$ ; cal.
1	330	603	0.000,26	9,880
2	370	643	0.001,02	8,800
3	410	683	0.003,75	7,580
4	450	723	0.011,10	6,465

Using

$$\Delta F_T = 8,800 \text{ at } 643^\circ\text{K.}$$

$$\Delta F_T = 6,465 \text{ at } 723^\circ\text{K.}$$

the following free energy equation as a linear function of temperature has been obtained:

$$\Delta F_T = 27,570 - 29.19T.$$

From the above equation the temperature of neutral equilibrium is  $T_0 = 671.5^\circ\text{C}$ . This shows that isoprene is more stable than 3-methyl-butene-1 above  $671.5^\circ\text{C}$ . Therefore, thermodynamically the favourable temperature of reaction for the formation of isoprene from 3-methyl-butene-1 at atmospheric pressure is above  $672^\circ\text{C}$ .