Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. II. Cracking Mechanism on the Pt-silica Gel Catalyst.

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In the previous paper the optimum analytical conditions were searched and found to lie within the definite ranges out of which the experimental values obtained were always lower than the calculated ones. We are going to explain the reasons for these by the experimental results and theoretical considerations.

I. Heating Rate of the Sample. When the rates of heating the sample are different the mean partial pressures of carbon oxides produced in the cracking zone will be also different; and slower the heating rate, more favourable it is for the complete reduction of carbon oxides. The temperature of the small outlet tube, on the inside wall of which the reduction water is condensed, is estimated to be around 40°–50°C. and, therefore, the mean partial pressure of water vapour produced and then the mean ratios of hydrogen to carbon monoxide and carbon dioxide are estimated to be around 14 and 25 respectively.

II. Cracking on the Pt-silica Gel Catalyst. (1) *Experimental Procedure.* The vapours produced from the sampling boat are normally heated to 950°C. on the Pt-silica gel catalyst and are completely decomposed to carbon monoxide, carbon dioxide and water vapour. The nickel catalyst which reduces the carbon oxides thus produced is removed from the reaction tube, intending to see the reaction course in the cracking zone. The water produced is caught by calcium chloride and the carbon dioxide by 50% potassium hydroxide solution.

(2) *Influence of Cracking Temperature.* The results on saccharose are given in Table 4.

Table 4. The influence of cracking temperature on the distribution of oxygen in the various products.

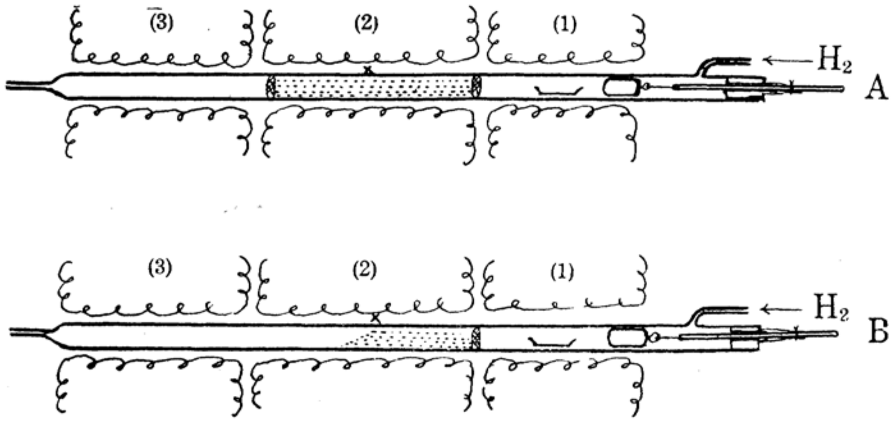
Sample saccharose (Oxygen % = 51.43), heating temp. of sample saccharose 950°C., hydrogen velocity 4 l./hr., analytical period, 60 min..

Expt. No.	Temp. of Pt-silica gel °C.	Sample g.	H_2O produced %	CO_2 produced %	Oxygen balance, %			
					to H_2O	to CO_2	to CO	Undecomposed
C–18	800	0.1526	30.34	5.77	52.38	8.17	37.04	2.41
C-32	850	0.1777	28.19	5.46	48.69	7.72	41.63	1.96
C–15	860	0.1668	27.04	4.98	46.68	7.04	44.32	1.96
C–16	860	0.1486	27.05	5.18	46.70	7.33	44.01	1.96

Table 4.—(*Concluded*)

Expt. No.	Temp. of Pt-silica gel °C.	Sample g.	H_2O produced %	CO_2 produced %	Oxygen balance, %			
					to H_2O	to CO_2	to CO	Undecomposed
C-21	880	0.1423	25.37	4.36	43.81	6.16	48.48	1.55
C-20	900	0.1676	24.82	3.58	42.85	5.06	50.54	1.55
C-22	950	0.1487	21.59	2.96	37.27	4.18	58.55	0
C-24	950	0.1332	21.25	2.78	36.69	3.93	59.38	0
C-3	* 950	0.1328	24.92	3.61	43.04	5.10	51.86	0
C-2	* 950	0.1154	25.41	3.47	43.87	4.91	51.22	0

* The cracking Pt-silica gel catalyst was inserted in the reaction tube as shown in Fig. 6-A, the other as in Fig. 6-B.



× : The position, at which the temperature was measured.

Fig. 6. Modes of Charging Pt-silica Gel Catalyst.

In the previous paper the percentage decompositions of oxygen of saccharose as a function of cracking temperatures were ascertained, and, therefore, percentage of carbon monoxide and that of oxygen remained undecomposed may be calculated, combining with the data here obtained.

The results of Table 4 show that the oxygen of saccharose is largely decomposed into water vapour and carbon monoxide, and the higher the cracking temperature, the more carbon monoxide and the less water vapour and carbon dioxide are produced. The different results of C-2, C-3 from those of C-22, and C-24 are easily explained through the different temperature distributions of cracking catalyst.

(3) *Influence of Streaming Velocity of Hydrogen.* The cracking catalyst was inserted as shown in Fig. 6-B and the influence of streaming velocity of hydrogen was examined and the results obtained were shown in Table 5.

Table 5. The influence of streaming velocity of hydrogen.

Sample saccharose, temp. of Pt-silica gel catalyst 950°C., analytical period 60 min..

Expt. No.	H_2 Vel. l./hr.	Sample g.	H_2O produced %	CO_2 produced %	CO (diff.) %	Oxygen balance		
						to H_2O	to CO_2	to CO
C-27	2.2	0.1641	22.48	4.20	28.09	38.81	5.93	55.26
C-25	3.0	0.1423	21.64	3.51	29.64	37.37	4.96	57.67
C-24	4.0	0.1332	21.25	2.78	30.52	36.69	3.93	59.38
C-28	4.8	0.1391	22.14	1.94	30.34	38.23	2.74	59.03

The rapid flow of hydrogen produced the decreased production of carbon dioxide and the increased production of carbon monoxide, while the amount of water approximately remaining constant.

(4) *Cracking of Other Several Organic Compounds.* Succinic acid, benzoic acid, and anthraquinone were examined for their cracking behaviour in the same way as in the case of saccharose. The results of Table 6 indicate that the sample which contained large amount of oxygen tends to give large amount of carbon dioxide, particularly at lower temperatures.

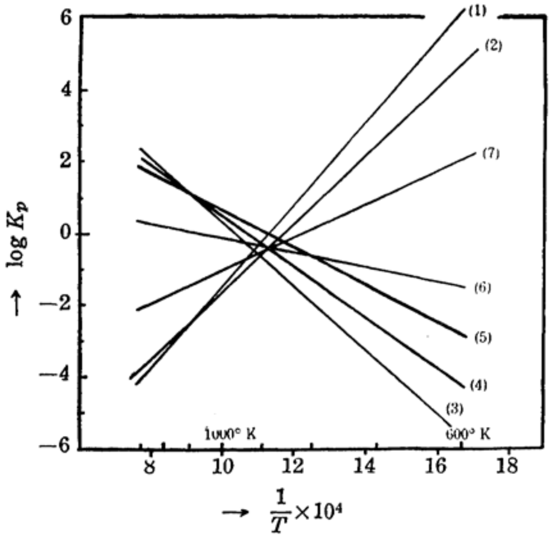
Table 6. The cracking of several organic compounds at various temperature.

Streaming velocity of H_2 4 l./hr., analytical period 60 min..

Expt. No.	Sample	Temp. of Pt-silica gel Catalyst °C.	Sample g.	H_2O produced %	CO_2 produced %	Oxygen balance		
						to H_2O	to CO_2	to CO
C-40	Succinic acid (0% = 54.22)	850	0.1405	15.94	18.93	26.11	25.40	—
C-41		860	0.2274	12.01	17.15	19.67	23.00	—
C-39		900	0.1809	10.17	10.06	16.65	13.50	—
C-38		950	0.1828	6.35	3.83	10.40	5.15	84.45
C 36	Benzoic acid (0% = 26.22)	800	0.1213	0.99	1.32	3.36	3.36	—
C-34		850	0.1240	0.56	1.29	1.90	3.55	—
C-35		900	0.1492	0.47	1.00	1.60	2.78	—
C-33		950	0.1317	0.30	0.68	1.03	1.87	97.10
C-42	Anthraquinone (0% = 15.37)	950	0.2757	0.22	0.22	1.27	1.04	97.69

(5) Discussion of Results. *Calculation of Oxygen Distribution Balance.* At the high temperatures as 800～950°C. all the organic compounds containing oxygen decompose and liberate their oxygen as carbon monoxide, carbon dioxide, and water vapour, and, therefore, the following several reactions have to be considered in the discussion of the results.

$$C + CO_2 = 2CO \quad \text{(3)}$$
$$C + H_2O = CO + H_2 \quad \text{(4)}$$
$$C + 2H_2O = CO_2 + 2H_2 \quad \text{(5)}$$
$$CO_2 + H_2 = CO + H_2O \quad \text{(6)}$$
$$C + 2H_2 = CH_4 \quad \text{(7)}$$



(1) $CO + 3H_2 = CH_4 + H_2O$
(2) $CO_2 + 4H_2 = CH_4 + 2H_2O$
(3) $C + CO_2 = 2CO$
(4) $C + H_2O = CO + H_2$
(5) $C + 2H_2O = CO_2 + 2H_2$
(6) $CO_2 + H_2 = CO + H_2O$
(7) $C + 2H_2 = CH_4$

Fig. 7. Relation between Equilibrium Constants and Reaction Temperatures.

The dependence of equilibrium constants Kp on the temperatures of these reactions are represented in Fig. 7. Reaction (5) is the combination of reaction (4) and (6) and is not necessary to be considered here. The Kp of reaction (3), (4), and (6) increase with temperature and, therefore, produce more carbon monoxide. The percentage distributions of oxygen in the products of reactions are calculated and plotted in Fig. 8–11 as a function of temperatures.

The reaction (3) occurs under approximately 1/10 atmosphere in our analytical conditions and consequently ought to give at equilibrium about 1% of carbon dioxide at 950°C. (Fig. 8). H_2/CO_2 being 10~20, the reaction (6) may produce 3–6% of

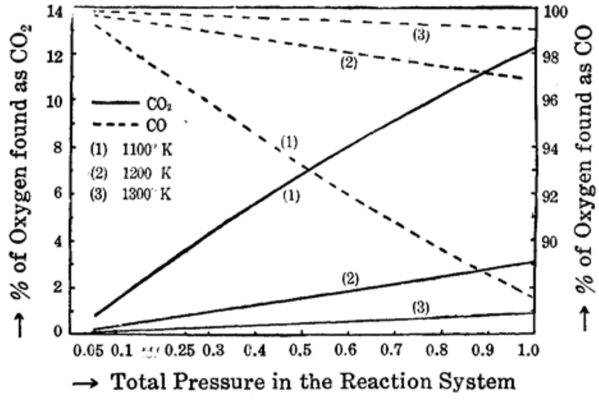


Fig. 8. Oxygen Balance in $C + CO_2 = 2CO$.

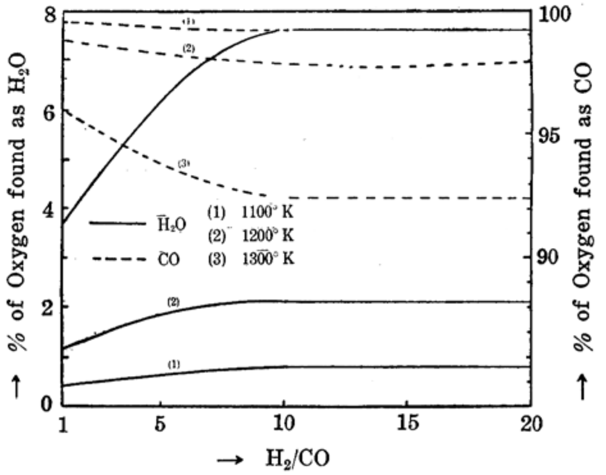


Fig. 9. Oxygen Balance in $C+H_2O = CO+H_2$.

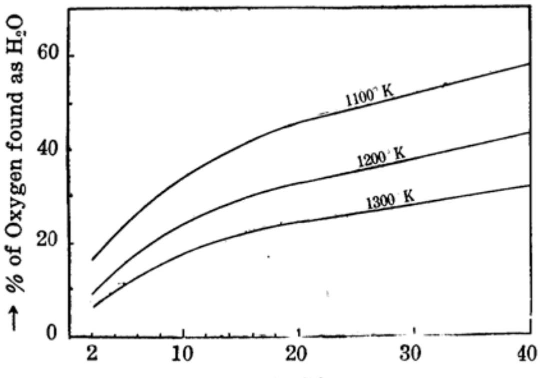


Fig. 10. Oxygen Balance in $C+2\,H_2O = CO_2+2\,H_2$

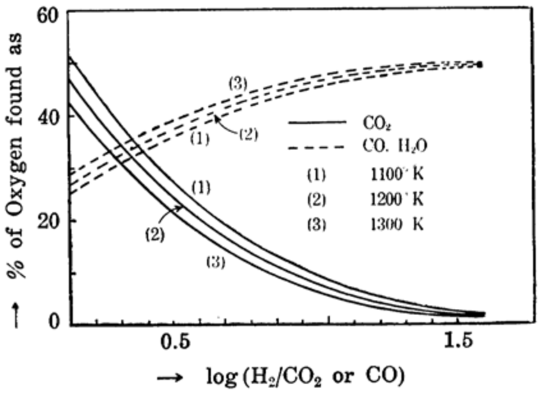


Fig. 11. Oxygen Balance in $CO_2+H_2 = CO+H_2O$.

carbon dioxide at 950°C. and the large proportion of oxygen in the sample will appear as carbon monoxide and water vapour. These estimations are quite concordant with our experimental results.

(6) *Reaction of Free Carbon with Carbon Dioxide.* The aromatic compounds produce on decomposition quite considerable amount of free carbon. The increase of streaming velocity of hydrogen reduces the mean partial pressures of carbon oxide and, therefore, drive the equilibrium point of reaction (3) toward the carbon monoxide side and reduces the carbon dioxide formation. On the contrary the decrease of hydrogen velocity favours the carbon dioxide formation. These considerations show good agreement with the experimental results given in Table 5. Succinic acid and saccharose give at 950°C. 3–4% of carbon dioxide and these are more than the equilibrium figures and, therefore, it is concluded that the cracked gases from the compounds which contain large amount

of oxygen pass through the cracking zone without reaching the equilibrium point.

(7) *Reaction of Free Carbon with Steam.* The water produced by the cracking reaction of the sample will react with the free carbon deposited in the cracking zone of reaction tube. The Fig. 9 indicates that 97% of water may decompose at 950°C. through the reaction (4). Succinic acid and saccharose which deposit only small amount of carbon give large amount of water and small amount of carbon monoxide. On the contrary the aromatic compounds like benzoic acid and anthraquinone which produce a considerable amount of carbon give nearly calculated amount of carbon monoxide and water (Table 6). Planning to prove these conclusion more definitely the surface of Pt-silica gel catalyst was purposely covered with free carbon and its behaviour was compared with that of the clean surface.

Table 7. Reaction of free carbon with H_2O or CO_2

Temp. of Pt-silica gel catalyst 950°C., H_2 velocity 4 l./hr.,
A cases, the catalyst was clean
B cases, the catalyst was covered with free carbon

Sample		Condition of catalyst	H_2O produced %	CO_2 produced %	Oxygen balance, %		
Kinds	g.				to H_2O	to CO_2	to CO
H_2O	0.1441	A	99.39	0	99.39	0	0.61
	0.0428	B	2.10	1.64	2.10	1.34	96.56
$NaHCO_3$*	0.2830	A	16.86 (10.72)	5.90 (26.19)	52.41 (33.34)	15.01 (66.66)	32.58 (0)
	0.2199	B	0.79 (10.72)	0.79 (26.19)	2.46 (33.34)	1.99 (69.66)	95.55 (0)

* The sample bicarbonate, on heating to 300°C. decomposed stoichiometrically, $2\,NaHCO_3 = Na_2CO_3+CO_2+H_2O$, and gave the products of figures in brackets.

The results of Table 7 prove quite conclusively the deduction discussed above. These data, furthermore, indicate that the presence of sufficient amount of free carbon produces the equilibrium mixture of cracked gases after the reaction (4).

(8) *Water-gas Reaction.* In order to decide whether the reaction (6) participates or not in the formation of water in the cracking zone, the behaviour of sodium oxalate which produces only carbon monoxide and carbon dioxide and no water was examined and the results obtained were given in Table 8. The degree of decomposition of sodium oxalate at 950°C. was found to be about 90.0% by the blank experiments. It is clear that the reaction (6) is also responsible for the formation of water and also that the reaction (6) does not reach the equilibrium point of these cases in which the initial concentration of carbon dioxide is exceedingly high.

Table 8. Cracking of sodium oxalate.

$$Na_2C_2O_4 = Na_2O + CO_2 + CO$$

Expt. No.	Sample g.	Temp. of Pt-silica gel catalyst °C.	H_2 Vel. l./hr.	Oxygen balance, %		
				to H_2O	to CO_2	to CO (diff.)
C-53	0.2037	800	3.8	27.66	21.68	50.66
C-52	0.2901	900	3.0	22.53	21.28	56.19
C-51	0.3183	950	4.0	22.93	19.56	57.51
C-50	0.2654	1000	3.5	22.44	10.41	67.15

(9) *Reaction of Free Carbon with Hydrogen.* The free carbon produced in the cracking zone may combine with hydrogen and disappear as methane; however, at such a high temperature as 950°C. the equilibrium of reaction (7) is unfavorable for the production of methane and, furthermore, the free carbon formed may be transformed into a stable form and loses its activity toward hydrogen; thus resulting in the accumulation of free carbon on Pt-silica gel catalyst in the cracking zone. It is, therefore, necessary to burn off the free carbon with air from time to time, usually after 7–10 analyses.

In conclusion, the mechanism of reaction in the cracking zone is satisfactorily explained by the occurrence of reactions (3), (4), and (6); the higher the cracking temperature the more carbon monoxide forms, and the rapid heating of the sample in the boat or high content of oxygen of the sample favours the increasing amount of carbon dioxide, thus exceeding equilibrium amount of carbon dioxide at the cracking temperatures. The mechanism of reduction of carbon monoxide and carbon dioxide thus formed will be discussed in the next paper.

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