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Abstract

Full Text

PHYSICAL CHEMISTRY

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STUDY OF THE KINETICS OF THE CATALYTIC OXIDATION OF PROPYLENE TO ACROLEIN BY THE FLOW-CIRCULATION METHOD

(Presented by Academician A. A. Balandin, 10 XII 1960)

A limited number of works have been devoted to the process of oxidation of propylene to acrolein on a cuprous oxide-copper contact (¹⁻⁵). The aim of the present study was to obtain data on the kinetics of this process using the flow-circulation method, the most suitable for this purpose (⁶).

In studying the influence of external diffusion, the procedure described earlier (⁷) was used. The data obtained, given in Table 1, show that

Table 1

Oxidation of propylene at different linear velocities L of the gas stream (flow rate 253 cm³/min; catalyst volume 4 cm³; [C₃H₆] = 22-24%; $t = 379^\circ$, Cu content 10 g per 1 l of catalyst)

L , m/sec	CO ₂ , %	C ₃ H ₄ O, %	O ₂ , %	$W_1 \cdot 10^7$, mole · sec ⁻¹ per 1 ml cat.	$W_2 \cdot 10^7$, mole · sec ⁻¹ per 1 ml cat.	X_{O_2} , %	$S_{C_3H_4}$, %
1.8	2.10	0.73	5.85	3.38	9.78	40	51
0.4	2.10	0.73	5.85	3.38	9.78	40	51

a change in the linear velocity by more than a factor of 4 has no effect on the rate of formation of acrolein (W_1) and carbon dioxide (W_2), the degree of conversion of oxygen (X_{O_2}), and the selectivity of the process ($S_{C_3H_4}$). Consequently, under our conditions the kinetic data were not distorted by phenomena of external transfer.

The kinetics of the process was studied on a contact containing 2.4 g Cu per 1 l. The carborundum support used, with grains of 2-3 mm, had large pores

(average diameter $6 \cdot 10^{-2}$ cm), which did not create intradiffusion difficulties; this was verified experimentally by the method of crushing the grains.

Some of the kinetic data obtained by us are presented in Table 2. From these data it is seen that the rates of formation of acrolein and carbon dioxide are proportional to the oxygen concentration and depend only weakly on the propylene concentration. At unchanged contents of the starting substances in the cycle, the rate decreases with increasing concentration of oxidation products, which indicates their inhibiting action.

The rates of formation of acrolein and carbon dioxide at constant propylene concentration are described by the following kinetic equations:

$$W_1 = \frac{k_1[\text{O}_2]}{1 + b\Delta[\text{O}_2]}, \quad W_2 = \frac{k_2[\text{O}_2]}{[\text{C}_3\text{H}_4\text{O}]^{0.7}}, \quad (1)$$

where $[\text{O}_2]$ is the concentration of oxygen in the cycle, $\Delta[\text{O}_2]$ is the decrease in oxygen concentration, calculated from the difference between the oxygen concentrations

in the feed mixture and its concentration at the outlet; k_1 , k_2 , and b are constants that depend on temperature. The term $b\Delta[\text{O}_2]$ in the equation is due to the inhibiting action of the products.

Table 2

Dependence of the rate of formation of acrolein (W_1) and carbon dioxide (W_2) on the oxygen and propylene content in the cycle and on the flow rate (catalyst volume 8 ml)

Flow rate, cm^3/min	O_2	C_3H_6	$\text{C}_3\text{H}_4\text{O}$	CO_2	$S_{\text{C}_3\text{H}_6}, \%$	$W_1 \cdot 10^7,$	$W_2 \cdot 10^7,$	$k_1 \cdot 10^7$	$k_2 \cdot 10^8$
						mole · sec ⁻¹ per 1 ml cat.	mole · sec ⁻¹ per 1 ml cat.		
Stationary conc. in cycle, %	Stationary conc. in cycle, %	Stationary conc. in cycle, %	Stationary conc. in cycle, %	Stationary conc. in cycle, %	Stationary conc. in cycle, %	$t = 335^\circ; b = 2.6$	$t = 335^\circ; b = 2.6$	$t = 335^\circ; b = 2.6$	$t = 335^\circ; b = 2.6$
1	1	1	1	1	1	1	1	1	1

Flow rate, cm ³ /min	O ₂	C ₃ H ₆	C ₃ H ₄ O	CO ₂	S _{C₃H₆} , %	W ₁ · 10 ⁷ , mole · sec ⁻¹ per 1 ml cat.	W ₂ · 10 ⁷ , mole · sec ⁻¹ per 1 ml cat.	k ₁ · 10 ⁷	k ₂ · 10 ⁸
258	3.05	97	0.19	0.17	76	0.455	0.408	0.07	0.09
303	6.15	94	0.30	0.20	81	0.845	0.565	0.08	0.09
279	13.85	95	0.51	0.35	81	1.325	0.908	0.08	0.09
229	5.70	51.8	0.33	0.27	79	0.702	0.575	0.08	0.10
278	5.90	24.4	0.28	0.27	76	0.723	0.697	0.08	0.11
285	5.80	11.45	0.24	0.35	67	0.640	0.927	0.07	0.13
Catalyst	Catalyst	Catalyst	Catalyst	Catalyst	Catalyst	Catalyst	Catalyst	Catalyst	Catalyst
2	2	2	2	2	2	2	2	2	2
561	6.05	22.8	0.24	0.26	73	1.252	1.355	0.12	0.19
291	5.95	23.5	0.34	0.36	74	0.920	0.974	0.11	0.17
142	5.95	23.9	0.49	0.60	71	0.647	0.795	0.11	0.17
141	5.90	23.5	0.44	0.62	68	0.576	0.814	0.10	0.18
84	5.80	22.9	0.60	1.00	65	0.470	0.777	0.12	0.20
t =	t =	t =	t =	t =	t =	t =	t =	t =	t =
365°; b =	365°; b =	365°; b =	365°; b =	365°; b =	365°; b =	365°; b =	365°; b =	365°; b =	365°; b =
3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85
531	6.00	23.6	0.43	0.55	71	2.13	2.73	0.48	0.59
308	5.90	22.7	0.50	0.90	63	1.43	2.58	0.46	0.63
148	5.90	22.5	0.68	1.50	58	0.94	2.06	0.46	0.63
69	5.80	22.0	0.91	2.40	53	0.586	1.54	0.43	0.57

The values of the rate constants k_1 and k_2 calculated from these equations are given in Table 2. The constancy of the constants, when the flow rate is varied by a factor of 7 and the oxygen concentration by a factor of 5, indicates the applicability of the indicated equations. The proposed equations do not contain the concentration of propylene, although, strictly speaking, the rate and selectivity of propylene oxidation depend on its content in the mixture.

With an increase in the propylene concentration the selectivity increases somewhat (Fig. 1). With small changes in the propylene content in the mixture, or with a considerable excess of it, the rate and selectivity remain constant, and the equations we propose are valid.

Dependence of the selectivity with respect to propylene ($S_{C_3H_6}$) on the concentration of propylene at 335° (1) and 365° (2), and at a constant oxygen concentration in the cycle equal to 6%.

Fig. 1. Dependence of the selectivity with respect to propylene ($S_{C_3H_6}$) on the concentration of propylene at 335° (1) and 365° (2), and at a constant oxygen

concentration in the cycle equal to 6%.

The activation heats calculated from the equations given above for the formation of C_3H_4O , E_1 , and of carbon dioxide, E_2 , in the interval 335–380° proved to be equal to

$$E_1 = E_2 = 36 \pm 2.5 \text{ kcal/mole}; \quad b = 4.25 \cdot e^{-10000/RT}.$$

To clarify the question of which of the products inhibits the reaction, a method was used in which certain products were removed from the cycle (8), while maintaining a constant concentration of the starting substances. From the data presented in Table 3 it is seen that, upon removal of acrolein and water, the reaction rate...

Table 3

Effect of reaction products on the rate of the process

(catalyst volume 8 cm³, [C₃H₆] = 19–21%)

Conditions	[O ₂] at outlet, %	O ₂	C ₃ H ₄	CO ₂	Products re- moved	S _{C₃H₆} , %	W ₁ ·	W ₂ ·
	10 ⁷ , mol · sec ⁻¹ per 1 ml cat.						10 ⁷ , mol · sec ⁻¹ per 1 ml cat.	
t = 335°, flow rate 280 cm ³ /min	6.85	5.90	0.29	0.30	—	74 ± 2	0.755	0.778
t = 335°, flow rate 280 cm ³ /min	7.65	5.95	0.05	0.85	C ₃ H ₄ O, H ₂ O	74 ± 2	1.94	2.22
t = 335°, flow rate 280 cm ³ /min	7.65	5.80	0.07	none	CO ₂ , H ₂ O, C ₃ H ₄ O	—	—	—

Conditions	[O ₂] at outlet, %	O ₂	C ₃ H ₄	CO ₂	Products re- moved	S _{C₃H₆} , %	W ₁ · 10 ⁷ , mol · sec ⁻¹ per 1 ml cat.	W ₂ · 10 ⁷ , mol · sec ⁻¹ per 1 ml cat.
t = 365°, flow rate 283 cm ³ /min	7.30	5.70	0.41	0.80	—	60 ± 1	1.07	2.01
t = 365°, flow rate 283 cm ³ /min	9.70	5.85	0.06	1.90	C ₃ H ₄ O, H ₂ O	67 ± 1	3.39	5.00
t = 365°, flow rate 283 cm ³ /min	9.70	5.95	0.05	none	CO ₂ , H ₂ O, C ₃ H ₄ O	—	—	—
t = 365°, flow rate 283 cm ³ /min	7.50*	5.70	0.45	0.90	—	60 ± 1	1.28	2.56
t = 365°, flow rate 283 cm ³ /min	8.25*	5.80	0.43	1.25	H ₂ O	—	—	3.57

* Flow rate 307 cm³/min.

tion increased by a factor of 2.5-3. When all products are removed, the degree of conversion of oxygen remains the same as when only C₃H₄O and H₂O are removed. Consequently, carbon dioxide has no noticeable effect on the reaction rate. When only water is removed and the acrolein concentration is unchanged, the rate of carbon dioxide formation increases by approximately a factor of 1.5.

The data obtained by us confirm the conclusion of O. V. Isaev and L. Ya. Margolis⁵ concerning the first-order dependence of the rate of propylene oxidation on the oxygen concentration. At the same time, they do not agree with the conclusion of the same authors regarding the absence of inhibition of the propylene oxidation process by reaction products and the complete absence of an effect of propylene.

It should be noted that the cited authors⁵ worked by the flow method, which, in studies of the kinetics of exothermic reactions, is less suitable than the flow-circulation method. At 335°, removal of acrolein from the cycle did not lead to an increase in selectivity, which should have occurred if its further oxidation were taking place. At 365°, as a result of freezing out C_3H_4O , the selectivity increases somewhat; consequently, at this temperature, under ordinary conditions, further oxidation of acrolein is possible. These data confirm the conclusion we made earlier⁴ that acrolein and carbon dioxide are formed predominantly in parallel at low temperatures, and that carbon dioxide is formed by a parallel-consecutive route at high temperatures.

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