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Abstract

Full Text

Physical Chemistry

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On the Yields of Formaldehyde and Acetaldehyde in the High-Temperature Oxidation of Ethane

(Presented by Academician N. N. Semenov, 30 VII 1957)

Concepts leading to the existence of limiting yields of stable intermediate products (SIP) in complex chain reactions ([1]) were tested on the example of methane oxidation ([1,2]). As an object for further testing of these concepts, the next representative, in order of complexity, of the homologous series of paraffin hydrocarbons—ethane—was chosen.

Fig. 1. Effect of additions of NO_2 and N_2 on the yield of aldehydes and on the manometric kinetics; $T = 512°$, pressure of the mixture $C_2H_6 : 2O_2$ 25 mm Hg; H_2F_2 vessel; dashed line—manometric kinetics; solid curves—kinetics of accumulation of CH_2O; dash-dotted line—kinetics of accumulation of CH_3CHO; $1, 1', 1''$—without addition; $2, 2', 2''$—with addition of 0.085% NO_2; $3, 3', 3''$—with addition of 0.33% NO_2; $4, 4', 4''$—mixture diluted with nitrogen 10-fold.

The behavior of the yields of two SIPs (formaldehyde and acetaldehyde) was studied under variation of the conditions of high-temperature oxidation of C_2H_6. The apparatus and method of work have been described previously ([1]). The presence in the polarographically analyzed solution of a mixture of two aldehydes introduced no complications into the analytical procedure, since both gave clearly separated waves in 0.05 N LiOH solution.

The experiments were carried out in two quartz reaction vessels, 45 mm in diameter and 250 ml in volume, with the walls treated by: 1) washing with H_2F_2 (H_2F_2 vessel) and 2) washing with 1% $K_2B_4O_7$ solution ($K_2B_4O_7$ vessel).

The results of experiments at low pressures (25 mm Hg) for mixtures relatively rich in oxygen ($C_2H_6 : 2O_2$) are shown in Fig. 1, from which it is seen that additions of a radical initiator (NO_2) and dilution of the reaction mixture with an inert gas (N_2) greatly increase the concentration of active centers in the reaction system, as may be judged from the strong increase in the rate of pressure

Fig. 2

Figure 2: Fig. 2

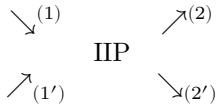
rise. The yields of CH_2O and CH_3CHO in this case practically do not change, i.e., they do not differ from the limiting yields ([1,2]).

The same experiments were repeated at a higher pressure, 53 mm Hg (see Fig. 2). The yield of CH_2O still did not change when the concentration of active centers was varied over wide limits and was approximately twice as high as the yield of CH_2O at a pressure of 25 mm Hg. With regard to the yield of CH_3CHO, however, we encountered an unexpected phenomenon: at the very end of the conversion, when the chain processes in the system were sharply inhibited, the rate of accumulation of CH_3CHO increased sharply ("jump") (which is especially clearly seen on curve 1 in Fig. 2), and the maximum concentration of CH_3CHO was reached at the moment when the rate of conversion according to Δp had already become equal to zero.

Fig. 2. Effect of additions of NO_2 and N_2 on the yield of aldehydes and on the manometric kinetics; $T = 512^\circ$; mixture pressure $C_2H_6 : 2O_2$ 53 mm Hg; H_2Fe vessel; $1, 1', 1''$—without addition; $2, 2', 2''$—with addition of 0.085% NO_2; $3, 3', 3''$—dilution of the mixture with nitrogen by a factor of 7. The remaining conventional designations are the same as in Fig. 1.

It is evident that at the moment when the rate according to Δp in the reaction system becomes equal to zero, the chain processes in it practically cease, since in high-temperature homogeneous oxidation of hydrocarbons in the gas phase CO is necessarily formed, which must be accompanied by an increase in pressure. Consequently, the maximum concentration of CH_3CHO reached after the "jump" cannot be regarded as the maximum yield of IIP in a complex chain reaction, and ideas about limiting yields are not applicable to it. It follows from this that the formation of CH_3CHO after the reaction has stopped according to Δp is due to some molecular reactions of the initial or intermediate substances.

Let us consider the question of the limiting yields of IIP in a complex chain reaction in which, alongside chain pathways of formation and consumption of IIP, there occurs not only molecular consumption of IIP [2], but also its molecular formation. Then the case under consideration may be represented in the form of the scheme



where the heavy arrows depict chain processes, and the light arrows—molecular processes. In this case it is necessary to distinguish the following three cases:

Fig. 3

Figure 3: Fig. 3

1) The steady-state concentration of the intermediate product (IPP) that would occur in the presence only of processes (1) and (2) (purely chain yield) is higher than the steady-state concentration that would occur in the presence only of processes $(1')$ and $(2')$ (purely molecular yield). Then any changes in the reaction conditions that promote an increase in the concentration of active centers in the reacting system (initiation, dilution of the mixture with an inert gas, etc.) will increase the yield of IPP, since with increasing concentration of active centers the role of processes (1) and (2) grows in comparison with processes $(1')$ and $(2')$, and the yield of IPP will consequently approach the purely chain yield.

2) The purely chain yield is lower than the purely molecular yield. Then an increase in the concentration of active centers in the reacting system will entail a decrease in the yield of IPP.

3) The purely chain yield practically does not differ from the purely molecular yield. Then variation of the reaction conditions affecting the ratio of the rates of the chain and molecular pathways of formation and consumption of IPP will not affect the yield of IPP.

Case 1) is practically impossible to distinguish from the case:

$$\longrightarrow \text{IPP} \lessgtr$$

observed in uninitiated or insufficiently initiated oxidation of methane ([2]), and case 3) from the case: $\longrightarrow$ IPP $\longrightarrow$, observed in sufficiently initiated oxidation of CH_4 ([1]).

Fig. 3. Influence of the nature of the surface of the reaction vessel and of additions of NO_2 and N_2 on the yield of aldehydes and on the manometric kinetics; $T = 452°$; mixture pressure $2C_2H_6 : O_2$ 53 mm Hg; $1, 1', 1''$—without addition in an H_2F_2 vessel; $2, 2', 2''$—dilution of the mixture with nitrogen by a factor of 5 in an H_2F_2 vessel; $3, 3', 3''$—with addition of 1% NO_2 in an H_2F_2 vessel; $4, 4', 4''$—with addition of 1% NO_2 in a $K_2B_4O_7$ vessel. The remaining symbols are the same as in Fig. 1.

The observed features of the kinetic behavior of CH_3CHO (the "jump" and the attainment of the maximum concentration at $d(\Delta p)/dt \simeq 0$) can be explained on the assumption that case 2 occurs here. Then it is obvious that, as long as the concentration of active centers in the system is sufficiently large, the concentration of CH_3CHO in the system tends to remain near the purely chain level. With a decrease in the concentration of active centers at the end of the conversion, the role of processes $(1')$ and $(2')$ increases in comparison with

Fig. 4. Effect of the surface of the reaction vessel and of NO_2 additions on the yield of aldehydes and on the manometric kinetics; T = 512°; pressure of the mixture $2C_2H_6$: O_2 53 mm Hg; 1,1′,1″ —without additive in the $K_2B_4O_7$ vessel; 2,2′,2″ —without additive in the H_2F_2 vessel; 3,3′,3″ —with addition of 1% NO_2 in the $K_2B_4O_7$ vessel. The remaining conditions and designations are the same as in Fig. 1.

Figure 4: Fig. 4. Effect of the surface of the reaction vessel and of NO_2 additions on the yield of aldehydes and on the manometric kinetics; T = 512°; pressure of the mixture $2C_2H_6$: O_2 53 mm Hg; 1,1′,1″ —without additive in the $K_2B_4O_7$ vessel; 2,2′,2″ —without additive in the H_2F_2 vessel; 3,3′,3″ —with addition of 1% NO_2 in the $K_2B_4O_7$ vessel. The remaining conditions and designations are the same as in Fig. 1.

processes (1) and (2), and the yield of CH_3CHO, increasing, tends toward the magnitude of the purely molecular yield. An increase in the concentration of active centers in the system should, from this point of view, always lead to a decrease in the "pre-jump" concentration of CH_3CHO. If the concentration of active cent-

of centers is sufficiently large that molecular processes can be neglected in comparison with chain processes, then the "pre-jump" yield of CH_3CHO will be the limiting yield. The results of the experiments shown in Fig. 3 indicate that dilution of the mixture with nitrogen and additions of initiator (1% NO_2) do indeed decrease the "pre-jump" yield of CH_3CHO; moreover, the yield of CH_3CHO in the initiated reaction does not change on going from the H_2F_2 vessel to the $K_2B_4O_7$ vessel, although the oxidation rate, as measured by Δp and serving as a measure of the concentration of active centers, decreases appreciably. This makes it possible to regard the value 0.03% CH_3CHO in the gas as the limiting yield for the given temperature, pressure, and mixture composition.

Fig. 4. Effect of the surface of the reaction vessel and of additions of NO_2 on the yield of aldehydes and on the manometric kinetics; $T = 512°$; pressure of the mixture $2C_2H_6 : O_2$ 53 mm Hg; $1, 1', 1''$ —without additive in the $K_2B_4O_7$ vessel, $2, 2', 2''$ —without additive in the H_2F_2 vessel, $3, 3', 3''$ —with addition of 1% NO_2 in the $K_2B_4O_7$ vessel. The remaining conditions and designations are the same as in Fig. 1.

The maximum yield of CH_3CHO ("post-jump"), as is seen from Fig. 3, does not undergo systematic changes with change in the concentration of active centers in the reaction system (as was also to be expected on the basis of the proposed interpretation).

From Figs. 3 and 4 it is evident that the yield of CH_2O in the case of mixtures $2C_2H_6 : O_2$ becomes a function of the reaction conditions: conditions that lead to an increase in the concentration of active centers in the system increase the yield of CH_2O. Treatment of the reaction vessel with a $K_2B_4O_7$ solution, just

as in the case of oxidation of CH_4 [2], decreases the reaction rate according to Δp in comparison with the H_2F_2 vessel. In the noninitiated oxidation of C_2H_6, the transition from the H_2F_2 vessel to the $K_2B_4O_7$ vessel is accompanied by a considerable decrease in the reaction rate and, simultaneously, by a strong drop in the yield of CH_2O (cf. curves $1'$ and $2'$, Fig. 4). In the initiated oxidation of C_2H_6, the yield of CH_2O practically does not change on going from the H_2F_2 vessel to the $K_2B_4O_7$ vessel (curves $3'$ and $4'$, Fig. 3), which makes it possible to regard the yield of CH_2O in this case as limiting. Thus, in the noninitiated oxidation of mixtures $2C_2H_6 : O_2$, in contrast to mixtures $C_2H_6 : 2O_2$, the rate of molecular consumption of CH_2O becomes comparable with the rate of its chain consumption, and the yield of CH_2O becomes lower than the limiting value. Under strong initiation the rate of the molecular path is immeasurably smaller than the rate of the chain path, and the yield practically does not differ from the limiting value.

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Note: Figure translations are in progress. See original paper for figures.