Soviet-era science, translated into English

Physical Chemistry

1958

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195801.95833

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

N. S. Enikolopyan and G. V. Korolev

Dependence of the Yields of Formaldehyde in the Oxidation of Methane on the Concentration of a Homogeneous Initiator, Additions of an Inert Gas, and on the State of the Walls of the Reaction Vessel

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

Earlier (^{1}) it was shown that the yield of a stable intermediate product (SIP) in a complex chain reaction, in which both the formation and the consumption of the SIP proceed only by a chain route, is not a function of the rate constants of initiation, termination, or degenerate branching of chains. This holds for any chain lengths in the case of spontaneous initiation of a "slow" active center; in the case of initiation of a "fast" active center, it holds only for sufficiently long chains.

The yield of the SIP, being a function only of the rate constants of the elementary chain-propagation reactions and of the concentrations of the initial and intermediate substances, does not depend on the diameter and nature of the walls of the reaction vessel, dilution of the mixture with an inert gas, or the concentration of the radical initiator, and is in this sense a limiting value. The existence of limiting yields of SIP in complex chain reactions has been experimentally confirmed using the example of homogeneous oxidation of methane (^{1}).

If, along with the chain route of consumption of the SIP, there is a molecular route comparable with it in rate, then the yield of the SIP in this case will be lower than the limiting value. In this case, a change in the reaction conditions that affects the ratio of the rates of the chain and molecular routes of consumption of the SIP will entail a change in the yield of the SIP. The results presented below of an experimental study of the yields of formaldehyde in the homogeneous oxidation of methane confirm this conclusion. The apparatus and procedure were described earlier (^{1}).

SovietRxiv

Fig. 2

Figure 2: Fig. 2

Fig. 1. Yield of CH_2O and increase in pressure during noninitiated oxidation of CH_4. Mixture $CH_4 : 2O_2$, pressure 150 mm Hg, temperature 512° C. 1, 2, 3, 4—curves of accumulation of CH_2O; $1'$, $2'$, $3'$, $4'$—manometric curves ($1'$ coincides with the abscissa axis); 1, $1'$—clean vessel; 2, $2'$—H_2F_2 vessel; 3, $3'$—$K_2B_4O_7$ vessel; 4, $4'$—H_2F_2 vessel and addition of N_2, 300 mm Hg.

Experiments on noninitiated oxidation of CH_4 were carried out in three quartz reaction vessels of the same diameter (45 mm), the surfaces of which were treated in different ways: 1) a vessel not subjected to any special treatment ("clean" vessel); 2) a vessel washed with hydrofluoric acid (H_2F_2 vessel); 3) a vessel washed with a 1% solution of $K_2B_4O_7$ ($K_2B_4O_7$ vessel).

The results of the experiments (Fig. 1) show that the yield of CH_2O depends on the state of the surface of the reaction vessel. Consequently, under the given conditions of CH_4 oxidation the yield of CH_2O is not limiting, i.e. the rate of mo-

the molecular consumption of CH_2O is commensurate with the rate of its chain consumption.

The observed dependence of the CH_2O yield on the nature of the surface of the reaction vessel may have two causes: 1) the destruction of active centers on the surface of the reaction vessel occurs in the kinetic or diffusion-kinetic region; 2) the heterogeneous reaction of CH_2O consumption proceeds in the kinetic or diffusion-kinetic region.

Fig. 2. Dependence of the maximum rate of oxidation of CH_4 and the yields of CH_2O on the concentration of the NO_2 additive. Mixture $CH_4 : 2O_2$, pressure 150 mm Hg, temperature 512°C. 1, 2, 3 –CH_2O yield; $1'$, $2'$, $3'$ –maximum rate according to Δp; 1, $1'$ –clean vessel; 2, $2'$ –H_2F_2 vessel; 3, $3'$ –$K_2B_4O_7$ vessel.

In the first case, a decrease in the effective constant of destruction, ϵ, of active centers on the surface upon passing from one vessel to another would lead to an increase in the stationary concentration of the active centers themselves in the reaction system, and this in turn would increase the fraction of chain consumption of CH_2O as compared with molecular consumption, as a result of which the value of the CH_2O yield will approach the limiting value, i.e., will increase. Obviously, if, upon passing from one vessel to another, ϵ increases, then the CH_2O yield will decrease owing to an increase in the fraction of molecular consumption of CH_2O as compared with chain consumption.

In the second case, with a decrease in the rate constant C of heterogeneous CH_2O consumption upon passing from one vessel to another, an increase in the CH_2O yield should be observed, owing to a decrease in the fraction of molecular

Fig. 3

Figure 3: Fig. 3

Figure 4

Figure 4: Figure 4

consumption of the aldehyde. Conversely, an increase in C entails a decrease in the $\mathrm{CH_2O}$ yield.

Obviously, dilution of the reaction mixture with nitrogen, by hindering the diffusion of radicals and $\mathrm{CH_2O}$ molecules to the wall, should increase the $\mathrm{CH_2O}$ yield if chain termination and the decomposition or oxidation of $\mathrm{CH_2O}$ at the wall (or at least one of these processes) proceeds in the diffusion or diffusion-kinetic region (dilution with nitrogen will decrease the apparent values of ϵ and C).

Fig. 3. $\mathrm{CH_2O}$ yield and pressure increase during oxidation of $\mathrm{CH_4}$ in the presence of various $\mathrm{NO_2}$ additives. Mixture $\mathrm{CH_4 : O_2}$, pressure 100 mm Hg, temperature 512°C, $\mathrm{K_2B_4O_7}$ vessel; 1, 2, 3, 4, 5 —curves of $\mathrm{CH_2O}$ accumulation; $1'$, $2'$, $3'$, $4'$, $5'$ —manometric curves. $\mathrm{NO_2}$ content in the mixture: 1, $1'$ –0.65%; 2, $2'$ –0.32%; 3, $3'$ –0.16%; 4, $4'$ –0.08%; 5, $5'$ –0.04%.

Indeed, the addition of 300 mm Hg of $\mathrm{N_2}$ to 150 mm Hg of a $\mathrm{CH_4 : 2O_2}$ mixture appreciably increases the $\mathrm{CH_2O}$ yield and the rate of pressure increase during oxi-

the decay rate, which is a measure of the concentration of active centers, in all three vessels. An especially significant effect upon dilution with N_2 was observed in the case of the H_2F_2-vessel (Fig. 1, curves 4 and $4'$).

It is also obvious that the addition to the reaction mixture of substances capable of generating active centers should increase the yield of CH_2O by increasing the share of the chain reaction as compared with the molecular one. When the concentration of radicals becomes so large that the molecular consumption of CH_2O constitutes only a negligibly small part of the chain consumption, the yield of CH_2O will reach a limiting value. A further increase in the concentration of active centers in the system can increase only the rate of oxidation, while the yield of CH_2O should then remain constant.

Fig. 4. Rate of oxidation of CH_4 and limiting yields of CH_2O upon initiation by additions of NO_2 and Cl_2. Mixture $CH_4 : O_2$, addition 36 mm Hg, temperature $610^\circ C$, $K_2B_4O_7$-vessel; 1, 2, 3, 4, 5, 6—curves of accumulation of CH_2O; $1'$, $2'$, $3'$, $4'$, $5'$, $6'$—manometric curves. Additive content in the mixture: 1, $1'$–0.13% NO_2; 2, $2'$–0.065% NO_2; 3, $3'$–0.02% NO_2; 4, $4'$–0.5% Cl_2; 5, $5'$–0.3% Cl_2; 6, $6'$—without additive.

Figure 2 presents the results of experiments on the oxidation of methane in the presence of various amounts of NO_2. It can be seen that increasing the NO_2 content in the mixture from 0 to 0.2-0.3% leads to an increase in the yield of CH_2O by a factor of 4-8; at the same time a strong increase in the oxidation rate is observed. In addition, it is seen that, as the NO_2 content in the mixture increases, the yield of CH_2O in all three vessels tends toward one and the same limiting value (0.75-0.80% CH_2O in the gas).

Unfortunately, it was not possible to trace the effect of NO_2 additions greater than 0.2-0.3%, since the maximum of the CH_2O concentration curve as a function of contact time, becoming narrower with increasing NO_2 concentration, at NO_2 additions above 0.2-0.3% becomes so sharp that the experimental errors in determining it become comparable with the possible increase of this maximum. Therefore, another series of experiments was carried out with NO_2 additions in mixtures with a lower oxygen content. From the curves in Fig. 3 it is seen that increasing the NO_2 concentration from 0.160 to 0.650%, while greatly increasing the oxidation rate, has practically no effect on the yield of CH_2O. At $[NO_2] < 0.162\%$, the yield of CH_2O becomes a function of the NO_2 concentration in the mixture.

Thus, at a sufficiently high concentration of active centers in the reaction system, the yield of CPP reaches its limiting value. It is obvious that the magnitude of the limiting yield of CPP will not depend on the manner in which this concentration of active centers is attained; it is only important that it be sufficient for an overwhelming predominance of the chain pathway of CPP consumption over the molecular one. In particular, if a sufficiently high concentration of chain carriers is created by introducing additions of an initiating impurity, the yield of CPP will not depend on the chemical nature of this impurity.

With the aim of experimentally verifying this conclusion, directly

arising from the concepts developed, two series of experiments were carried out in parallel: the reaction initiated by NO_2 and the reaction initiated by Cl_2. The results of these experiments are shown in Fig. 4, from which it is evident that varying the concentration of the initiator, while strongly affecting the rate of oxidation, has practically no effect on the yield of CH_2O; it follows from this that the oxidation proceeds in the limiting region. The yield of CH_2O when initiated by NO_2 lies within the range of 0.64–0.74% CH_2O in the gas (curves 1, 2, 3), and when initiated by Cl_2 it is 0.64% CH_2O in the gas, so that in both cases the limiting yield may be regarded as practically the same. For comparison, the yield of CH_2O (Fig. 4, curve 6) and the rate (curve 6′) of the uninitiated reaction under the same conditions are given.

Thus, the totality of the results presented above shows that, in the uninitiated oxidation of methane, there is a molecular pathway for the consumption of formaldehyde, the rate of which is comparable with the rate of its chain consumption; as a result, the yield of CH_2O in uninitiated oxidation is a function of the reaction conditions (the condition of the walls of the reaction vessel, dilution with an inert gas, etc.) and is several times lower than the limiting value. With an increase in the concentration of active centers in the reaction system, the yield of CH_2O rises to the limiting value, which no longer depends either on the condition of the walls of the reaction vessel or on the nature and concentration of the free-radical initiator.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
30 VII 1957

REFERENCES CITED

1. N. S. Enikolopyan, G. V. Korolev, G. P. Savushkina, *ZhFKh*, **31**, No. 4 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.