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Abstract

Full Text

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PHYSICAL CHEMISTRY

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THE INITIATING ACTION OF NITROSYL CHLORIDE IN THE OXIDATION OF PROPANE

In studying new ways of carrying out processes for the oxidative conversion of gaseous hydrocarbons in order to obtain valuable oxygen-containing substances, we have made extensive use in our investigations of the phenomenon of homogeneous catalysis and the principle of transferring high-molecular gas-phase reactions to regimes of mild low-temperature oxidation at temperatures and pressures close to the critical ones ([1,2]).

In both cases the aim was to lower the temperature at which the reaction is carried out and thereby reduce the fraction of useless combustion of hydrocarbons. In work ([2]) the action of several homogeneous catalysts and their mixtures was considered. In a number of subsequent studies a more detailed investigation was made of the chemical possibilities and the mechanism of action of homogeneous catalysts ([3–5]).

Among various homogeneous additives (initiators), our attention was attracted by nitrosyl chloride, NOCl–a very effective stimulator of oxidation processes, which exerts its action by a mechanism involving macroscopic stages separated in time ([6]).

Fig. 1. Kinetic curves of the change in pressure in the reaction of propane oxidation at $T = 250°$ and $P = 250$ mm.

Fig. 2

Figure 2: Fig. 2

1—125 mm C_3H_8 + 125 mm O_2; 2—120 mm C_3H_8 + 120 mm O_2 + 10 mm NOCl.

The elementary mechanism of the stimulating action of nitrosyl chloride apparently consists in the easy decomposition of NOCl into two active particles (NO and Cl), owing to the comparatively small value of the bond energy N—Cl, which is equal to 38 kcal/mol ([7]). The present work is devoted to a more detailed characterization of the action of NOCl additives in the propane oxidation reaction and to a comparison of it with the action of NO_2 additives.

In this connection we were mainly interested in the yield of such important oxygen-containing products as acetaldehyde and formaldehyde.

The oxidation was carried out in a static apparatus at 250° and a total mixture pressure of 250 mm Hg. Because of the low temperature, the reaction proceeded rather slowly (minutes). Since in the present work we did not set ourselves the task of selecting the optimum conditions for obtaining acetaldehyde and formaldehyde, the question of the reaction rate is not essential for us. The effect of the stimulating action of additives is manifested quite distinctly under these conditions.

First of all, this effect can be seen from the curves of pressure change during oxidation (Fig. 1). Incidentally, the character of the kinetic curve of pressure change upon additions of NOCl indicates the presence of macroscopic staging of the process. Indeed, the existence of macroscopic stages in the oxidation of propane in the presence of NOCl is confirmed by recording the heating of the reacting mixture during the reaction (Fig. 2).

Fig. 2. Photographic recording of the heating of the reacting mixture of propane and oxygen in the presence of 10 mm NOCl, $T = 285^{\circ}$ and $P = 250$ mm

It should be noted that the stimulating action of NOCl is clearly manifested also in the lowering of the autoignition temperature of mixtures of propane with oxygen. The peninsula of ignition of mixtures of propane, oxygen, and NOCl shifts into the region of lower temperatures—by about 100°.

From data on the temperature dependence of the rate of pressure change in the temperature region 230—270°, we determined the activation energy of the process of propane oxidation in the presence of NOCl, equal to 30 kcal/mole.

It is very significant that additions of NOCl increase not only the rates of formation, but also the maximum concentrations of the principal reaction products —acetaldehyde and formaldehyde—as compared both with the yields of these

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

substances in uninitiated oxidation and when nitrogen dioxide is used as a homogeneous gas initiator (Fig. 3).

Fig. 3. Kinetic curves of accumulation of formaldehyde (1) and acetaldehyde (2) in the reaction of uninitiated oxidation of propane with additions of 10 mm NOCl (curves 1 and 2) and 10 mm NO_2 (curves 1′ and 2′), $T = 250°$, $P = 250$ mm

Fig. 4. Kinetic curves of accumulation of nitropropane (1) and consumption of NOCl (2) in the reaction of oxidation of C_3H_8 initiated by additions of 10 mm NOCl (1 and 2) and by additions of 10 mm NO_2 (1′)

The main nitrogen-containing product of the reaction in the catalysis of the propane oxidation process by nitrosyl chloride and nitrogen dioxide is nitropropane. Comparison of the kinetic curves of NOCl consumption and $C_3H_7NO_2$ formation (Fig. 4, 1, 2) shows that practically all the bound nitrogen contained in NOCl passes into nitropropane.

The amounts of nitropropane at equal additions of NOCl and NO_2 are equal to one another, although the rate of formation of $C_3H_7NO_2$ under catalysis by nitrosyl chloride ···

with nitrosyl chloride than in the case of NO_2. From the equality of the maximum yields of nitropropane under catalysis by NOCl and NO_2, certain conclusions may be drawn about the mechanism of action of NOCl.

If the catalytic effect were reduced solely to the action of NO_2 formed upon dissociation of the NOCl molecule—as is assumed, for example, for the reaction of hydrogen with oxygen sensitized by NOCl—then the same action of NOCl and NO_2 should have been observed in the systems under consideration.

In reality, however, the catalytic effect of NOCl greatly exceeds the effect of equivalent amounts of NO_2. Consequently, in catalysis by NOCl, an important role in the initiation of oxidation chains is also played by Cl atoms formed during the decomposition of nitrosyl chloride.

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