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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Chemistry

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THREE TYPES OF KINETIC CURVES FOR THE INTERACTION OF METHANE AND PROPANE WITH NITROGEN DIOXIDE

The kinetics of vapor-phase nitration of methane and propane by nitrogen dioxide was studied in a vacuum apparatus equipped with a self-recording photocolorimeter for recording the consumption of nitrogen dioxide and a membrane manometer with photographic recording on a rotating drum for recording the increase in pressure. The reaction cylindrical vessel, with plane-parallel optical plates sealed into its ends, was made of quartz ($d = 45$ mm; $l = 235$ mm) in the case of methane and of molybdenum glass ($d = 50$ mm, $l = 200$ mm) in the case of propane. The reactor was placed in a tubular electric furnace with a constant temperature field along the length of the reactor, having a horizontal cutout for visual observation. The furnace temperature was maintained by a thermoregulator and measured with a thermocouple at the outer wall of the reactor. The purity of methane (not less than 99.5%) and propane (not less than 99.8%) was determined chromatographically. To carry out the reaction, a previously prepared mixture of alkane with nitrogen dioxide, taking into account the degree of dissociation of N_2O_4, was admitted from a transfer flask into the heated reactor.

Fig. 1. Three types of kinetic curves. Mixture $4CH_4 + NO_2$, 475°. a—slow reaction, b, c—reaction with a peak, d—reaction with ignition. The hatched and dashed lines show the region of influence of the inertia of the recording instruments. 1—P_{NO_2}, 2—ΔP

Depending on the composition of the mixture, the initial pressure, and the temperature, we observed three types of reaction course:

Fig. 2

Figure 2: Fig. 2

a) **Slow reaction** (Figs. 1a, 2a). It is characterized by a continuous increase in the total pressure up to saturation. At the same time, a corresponding, also continuous, consumption of NO_2 is observed. A distinctive feature of the kinetics is the constancy of the rate of NO_2 consumption up to the moment when it has been consumed by 30-50% (Fig. 2a). In the case of propane, at low temperatures (250-300°), low initial pressures, and mixture compositions $C_3H_8 : NO_2$ of 1 : 1, 2 : 1, and 4 : 1, the pressure-increase curve has an S-shaped form (Fig. 2a), and then in the initial moments of the reaction (sometimes up to 30-40 sec.) the total pressure remains practically constant, despite the rapid consumption of NO_2 observed during this period. This may be explained by the reaction proceeding in the initial stages without a change in volume. In the case of the interaction of methane with NO_2, such constancy of the total pressure in the initial moments of the reaction was not observed.

b) **Reaction with a peak** (Figs. 1 , 1 , 2). With an increase in the initial pressure or temperature, at constant mixture composition, the "slow reaction" changes into a "reaction with a peak." After an interval of time, varying depending on the initial conditions from 1.5 to 7 sec., during which a self-accelerating reaction is observed, there occurs a rapid pressure jump, during which, depending on the height of the peak, practically complete or considerable consumption of NO_2 takes place. The jump

Fig. 2. Three types of kinetic curves. Mixture C_3H_8 + NO_2, 300°. a —slow reaction; —reaction at the boundary between the slow reaction and the reaction with a peak; —reaction with a peak; —reaction with ignition. The designations are the same as in Fig. 1.

Table 1

Composition of the principal carbon-containing products at the moment of NO_2 consumption for the three types of kinetics (in mm Hg of C_3H_8 consumed)

Conditions	$\frac{RCHO + CO_2 + CO}{RNO_2}$	$\frac{CH_4 + C_{nH_{2n}}}{RNO_2}$
Slow reaction		
C_3H_8 + NO_2, 300°, P_{init} 327 mm *	$\frac{1.4 + 6.4 + 6.4}{13.7} = 1.0$	$\frac{2.7 + 0}{13.7} = 0.20$
C_3H_8 + $2NO_2$, 300°, P_{init} 320 mm *	$\frac{0.9 + 4.7 + 8.9}{23.8} = 0.61$	$\frac{0.9 + 0.9}{23.8} = 0.10$

Figure 3. Regions of the three types of kinetics of methane nitration.

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Conditions	$\frac{RCHO + CO_2 + CO}{RNO_2}$	$\frac{CH_4 + C_{nH_{2n}}}{RNO_2}$
Reaction with a peak		
$2C_3H_8 + NO_2$, 350°, P_{init} 318 mm *	$\frac{2.7 + 2.0 + 3.8}{11.9} = 0.71$	$\frac{1.3 + 2.0}{11.9} = 0.27$
$C_3H_8 + NO_2$, 300°, P_{init} 396 mm *	$\frac{3.7 + 5.5 + 8.9}{11.0} = 1.6$	$\frac{1.1 + 2.2}{11.0} = 0.30$
Reaction with ignition		
$C_3H_8 + 2NO_2$, 350°, P_{init} 171 mm *	$\frac{0.5 + 2.3 + 12.4}{0.1} = 150$	$\frac{9.6 + 12.6}{0.1} = 220$
$C_3H_8 + NO_2$, 300°, P_{init} 440 mm *	$\frac{7.5 + 5.2 + 15.3}{0.9} = 30$	$\frac{9.1 + 28.0}{0.9} = 40$

* Initial pressure of the mixture.

the pressure is not associated with the appearance of a visible flame. The pressure jump is followed by a sharp drop, sometimes (in the case of propane) to the initial pressure, after which a further slow increase of pressure up to saturation is observed. Figure 2b shows kinetic curves of the reaction at the boundary between the "slow reaction" and the "reaction with a peak."

c) **Reaction with ignition** (Figs. 1c, 2c). With a still greater increase in the initial temperature and pressure, the self-accelerating reaction passes into a distinct explosive process. In this case

Fig. 3. Regions of the three types of kinetics of methane nitration. 1 —slow reaction, 2 —reaction with a peak, 3 —reaction with ignition

Fig. 4. Regions of the three types of kinetics of propane nitration. The designations are the same as in Fig. 3

the entire reaction practically ends in a flame, during the passage of which all

Figure 4. Regions of the three types of kinetics of propane nitration.

Figure 4: Figure 4. Regions of the three types of kinetics of propane nitration.

the NO_2 is consumed. The intensity of the glow in this type of reaction increases, at constant temperature, with the initial pressure, and the color changes from pinkish-blue to white-yellow. At low initial pressures, propagation of the luminous front was observed from the center of the reactor, where the reacting mixture was introduced, to the ends of the reactor. The rate of propagation in this case is 15-20 cm/sec. A weak glow near the boundary of the region can be detected visually only in a dark room; it resembles the cold flames of slow oxidation of hydrocarbons. We were unable visually to observe luminescence, i.e., a nonpropagating glow, of which Joffe speaks [1].

The ratio of the pressure increase at the moment of NO_2 consumption to the initial pressure of NO_2 in the mixture, $\Delta P_1/P_{\text{initial, NO2}}$, for the reaction between CH_4 and NO_2 within a given mixture does not depend on the type of reaction kinetics, the initial pressure, or the temperature, and changes only slightly with the composition of the mixture. For compositions 2 : 1, 4 : 1, and 6 : 1 this ratio is equal to 0.41, 0.43, and 0.36.

The ratio $\Delta P_1/P_{\text{initial, NO2}}$ for the reaction between C_3H_8 and NO_2 is determined by the type of reaction kinetics and by the composition of the mixture. This ratio is minimal for the reaction with an intense peak (0.14 for 2 : 1, 400°; 0.12 for 2 : 1, 350°; 0.04 for 4 : 1, 400°), and maximal for the reaction with ignition (0.75 –

0.87 for 1 : 1 and 1 : 2) and has an intermediate value for the slow reaction (0.22–0.30 for 2 : 1 and 4 : 1 and temperatures from 250 to 400° and 0.38–0.46 for 1 : 1 and 1 : 2 and temperatures from 250 to 400°).

As is evident from the data in Table 1, the compositions of the products of the slow reaction and of the reaction with a peak are close to one another, but differ significantly from the composition of the products of the reaction with ignition.

Figs. 3 and 4 show the boundaries of regions with different types of kinetics. The boundary of the region of the reaction with a peak for CH_4 and C_3H_8 narrows with increasing temperature and with enrichment of the mixture in NO_2. Thus, for example, for the composition $CH_4 + 2NO_2$ (400–600°) no reaction with a peak was detected; for the composition $2CH_4 + NO_2$ (500°) the reaction with a peak occurs in the region P_{initial} 99–102 mm, and for the composition $4CH_4 + NO_2$ (500°) in the region P_{initial} 195–247 mm.

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CITED LITERATURE

1. A. D. Joffe, Res., 6, 11 S (1953).

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