Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962, Volume 144, No. 1

PHYSICAL CHEMISTRY

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STUDY OF THE KINETIC REGULARITIES OF COMPLEX CHAIN PROCESSES IN OPEN SYSTEMS AS A METHOD FOR DETERMINING THE RATES OF FORMATION AND CONSUMPTION OF INTERMEDIATE PRODUCTS

Processes of liquid-phase oxidation of hydrocarbons lead to the formation of various oxygen-containing compounds (peroxides, alcohols, ketones, acids), many of which are intermediate substances and, in the course of the reaction, undergo further transformations ([1]).

To establish the mechanism of hydrocarbon oxidation it is necessary to know the sequence of formation of the reaction products in the system and the rates of their formation and consumption during the process. Until now, for carrying out such studies the kinetic isotope method has been used, which requires the presence of "labeled" compounds and the ability to isolate intermediate substances in pure form from a complex mixture of oxidation products ([2]). As a result, the possibilities for applying the kinetic isotope method in liquid-phase oxidation reactions often turn out to be very limited. Meanwhile, carrying out consecutive reactions under open-system conditions provides a simple and convenient method for determining the rates of formation and consumption of intermediate substances. It is known that open systems are characterized by the establishment of a certain stationary concentration of reaction products, which depends on the rate of supply of the starting substance and does not depend on the concentration of the products at the moment of transition to the continuous regime ([3]). In a simple consecutive reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

the stationary concentrations of the intermediate and initial substances prove to be connected by the algebraic equation

$$k_1[\mathrm{A}]_i^n - k_2[\mathrm{B}]_i^{n_1} - \frac{v_i}{V}[\mathrm{B}]_i = 0. \tag{1}$$

Here $[\mathrm{A}]_i$ and $[\mathrm{B}]_i$ are the stationary concentrations of the initial and intermediate substances, v_i is the rate of withdrawal of the intermediate substance, and V is the volume of the vessel. Carrying out the reaction at various v_i, we obtain a system of equations of the form (1), making it possible to determine both the constants k_1 and k_2, and the quantities n and n_1 ([4,5]). This method has been used in only one work to determine the rate constants for the bromination of acetone ([6]).

In complex chain processes, when the concentration of radicals [R] is unknown, these relationships cannot be used to determine the rates of formation and consumption of intermediate substances. Indeed, the rate of accumulation of an intermediate substance in a chain reaction under open-system conditions can be written in the form

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{R}][\mathrm{A}] - k_2[\mathrm{R}][\mathrm{B}] - \frac{v}{V}[\mathrm{B}] = 0.$$

Since a change in the value of v leads to a change in the concentration of radicals R, determination of k_1 and k_2 becomes impossible.

To determine the rates of formation and consumption of substance B, in the present work we propose maintaining a constant concentration of radicals, i.e., of the initiating substance, while at the same time changing the stationary concentration of substance B. This can be achieved by feeding into the vessel not the pure initial substance, but its mixture with B at a definite concentration; moreover, the value of v in experiments with the addition of B and without the addition must be one and the same.

In this case, since the feed rate of the starting substances remains constant, the stationary concentrations $[A]$ and $[R]$ must also be constant*, and the stationary concentrations of product B in experiments without additions of B and with additions of B are determined by the equations:

$$k_1[R][A] - k_2[R][B] - \frac{v}{V}[B] = 0,$$

$$k_1[R][A] - k_2[R][B]_1 - \frac{v}{V}[B]_1 + \frac{v}{V}[B]_0 = 0.$$

The solution of this system of equations gives

$$\left(1 + \frac{k_2[R]V}{v}\right) = \frac{[B]_0}{[B]_1 - [B]}. \tag{2}$$

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Thus, for a first-order reaction, by plotting the dependence of $[B]_0$ on $[B]_1 - [B]$, one can calculate from the slope of the straight line the value of

Fig. 1. Kinetic curves of the accumulation of hydroperoxides (1) and acids (2) during the oxidation of n-decane in an open system in experiments with the feed of pure n-decane (a) and of mixtures of n-decane with decanol-2 in amounts of 0.207 mol/l (b) and 0.296 mol/l (c). The arrow indicates the moment at which the concentration of the alcohol being fed was changed.
$T = 140^\circ$

Fig. 2. Kinetic curves of the accumulation of alcohols during the oxidation of n-decane in an open system. For the designations, see the caption to Fig. 1.
$T = 140^\circ$

$k_2[R]$, and then the value $k_1[R]$, i.e., obtain the ratio k_1/k_2. If substance B is consumed according to the n-th order, formula (2) takes the form

$$\frac{k_2[R]V}{v} = \frac{[B]_0 + [B]^n - [B]_1^n}{[B]_1 - [B]}. \tag{3}$$

It should be noted that if several isomers are formed in the reaction, then, by feeding one of them into the system and analyzing the sum of the isomers, one can determine $k_2^i[R]$ for the given isomer. In other words, the method makes it possible to determine the relative reactivity of the isomers.

The rate of formation of the sum of isomers in this case can be obtained if the ratio of isomers in the product is known. If, however, the analytical methods used in the work make it possible to determine the concentration of each isomer separately, then the values of the rates of formation for all the isomers can also be calculated.

In the present work, the proposed method for determining the rates of formation and consumption of intermediate products was applied to the determination of the rates of formation and consumption of alcohols in the oxidation reaction of n-decane. The oxidation was carried out with oxygen at $T = 140^\circ$, with an O_2 feed rate of 1.6 l/h and an n-decane feed rate of

$$\frac{v}{V} = 2.9 \cdot 10^{-3}\ \mathrm{min}^{-1}.$$

The stationary concentration of peroxides during the oxidation of decane in an open system when feeding pure decane and decane containing 0.207 and 0.296 mol/l

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

* The method is applicable only in the case where introducing intermediate substance B does not substantially affect the rate of initiation or chain termination.

decanol-2 does not change (Fig. 1, curve 1). Since hydroperoxides are the main source of radicals in the oxidation of *n*-decane, the constancy of the hydroperoxide concentration indicates that, under the conditions of our experiments, the radical concentration does not change upon introduction of decanol-2.

Fig. 3. Dependence of the change in the stationary concentration of alcohols in experiments with the feed of pure *n*-decane (C_{st}) and of a mixture of *n*-decane with alcohol (C) on the concentration of the supplied decanol-2 (2) and nonanol-5 (1)

In Fig. 2 is shown the change in the concentration of alcohols in an experiment without addition of alcohol and with addition of 0.207 and 0.256 mole/liter decanol-2.

From the dependence of C_0 on $C - C_{\text{st}}$ (Fig. 3, 2), the quantity $k_2[\text{R}] = 2.3 \cdot 10^{-3}\ \text{min}^{-1}$ was determined. Here C_0 is the concentration of decanol-2 in the decane being fed, and C and C_{st} are the stationary concentrations of alcohols in experiments with and without addition of decanol-2. Analogous experiments were carried out with nonanol-5. The points fit well on a straight line in the coordinates C_0 and $C - C_{\text{st}}$, and give the value $k_2[\text{R}] = 1.7 \cdot 10^{-3}\ \text{min}^{-1}$.

The good linear dependence in both cases confirms the assumption that alcohols in the oxidation reaction of *n*-decane are consumed by a first-order reaction with respect to the alcohol, and is an additional indication that the alcohol does not exert a substantial influence on the radical concentration in the system.

Using the value of $k_2[\text{R}]$ found for decanol-2, and taking into account that the chain decomposition of the peroxide imitates a first-order reaction, it is possible to determine the value

$$k_1[\text{R}] = 6.1 \cdot 10^{-3}\ \text{min}^{-1}$$

and the ratio $k_1/k_2 = 2.5$.

Fig. 4. Kinetic curves of the accumulation of ketones during the oxidation of decane in an open system. For the notation see the caption to Fig. 1. $T = 140°$

The study of the stationary concentration of acids (Fig. 1, 2) and ketones (Fig. 4) showed that introduction of alcohol does not affect the stationary concentration of acids and increases the concentration of ketones. This makes it possible to conclude that ketones apparently are formed from alcohols, whereas acids are not formed to any noticeable extent either from alcohols or from ketones.

Thus, the study of the kinetic features of the course of complex chain processes in open systems is a simple and convenient method for determining the rates of formation and consumption of intermediate reaction products.

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Received
27 I 1962

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