

Procedure for Studying the Steady-State Kinetics of Oxidation of Gaseous Substrates by Hydrogen Peroxide in a Liquid Phase

A. O. Kuzmin and V. N. Parmon

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—A procedure was developed for studying the steady-state kinetics of oxidation of various gaseous substrates by hydrogen peroxide under conditions of the continuous release of gaseous products. The steady state of a system was provided by continuously injecting hydrogen peroxide at low conversions of the oxidized substrate. The process was monitored by measuring substrate losses in a gas phase rather than the buildup of products. This allowed us to avoid difficulties associated with further oxidation of the products.

INTRODUCTION

Catalytic oxidation reactions in solutions are usually multistage reactions. However, only the rate-limiting step of a process is often of profound interest. This step manifests itself most clearly in the steady-state occurrence of reactions. A standard approach to studying the kinetics of hydrocarbon oxidation in solutions consists in an investigation of the rate of product buildup or oxidant consumption. This approach may result in considerable errors because of the possibility of nonselective oxidant consumption and the secondary oxidation of products in side reaction steps.

The kinetic distribution method was developed in detail [1] for studying the reaction kinetics of oxidation of gaseous hydrocarbons by various oxidants in solutions. This method is based on the measurement of substrate losses in a gas phase under conditions of substrate distribution and transfer between a liquid and a gas. Rudakov [1] mistakenly stated that the procedure is fully non-steady-state, and it provides an opportunity to study the first step of substrate entering into reaction, for example, via complexation with a catalyst. In the majority of cases, this is not true, and the rate-limiting step of a process is studied with the use of this method. However, as applied to a study of the rate-limiting step of a process, the above method exhibits considerable advantages in a number of cases, because it cannot provide a steady state in the catalytic system. This is due to the great change in the concentration of an oxidant in the course of reaction. This method does not take into account the possible dilution of a gas phase with oxygen, which is released in the course of the side reaction of hydrogen peroxide decomposition.

We developed a procedure for studying the steady-state kinetics of oxidation of gaseous hydrocarbons; this procedure avoids the above disadvantages. This procedure is described below with a detailed analysis of errors that appear with the use of this procedure.

EXPERIMENTAL PROCEDURE

We propose to study the kinetics of oxidation of a gaseous hydrocarbon with hydrogen peroxide in a system that includes a catalytic reactor like a long-necked flask. A liquid oxidant (hydrogen peroxide) is continuously injected into this reactor at a constant flow rate. In this case, if the rate of the side reaction of oxidant decomposition with the release of oxygen in the system is much higher than the rate of substrate oxidation (this is true at low rates of oxidation or at low substrate concentrations), the system reaches a steady state with a constant concentration of hydrogen peroxide in solution. The volume of released oxygen is changed with time; this fact makes it possible to take into account dilution in the gas phase of the reactor. In addition to an oxidized hydrocarbon, an inert gaseous standard substance, for example, methane which is difficult to oxidize, is introduced into the system. In the course of an experiment, the substrate-to-standard concentration ratio is determined by gas chromatography. This procedure provides a high accuracy of measurements; as a result, for example, the apparent rate constant and the order of oxidation reaction can be determined.

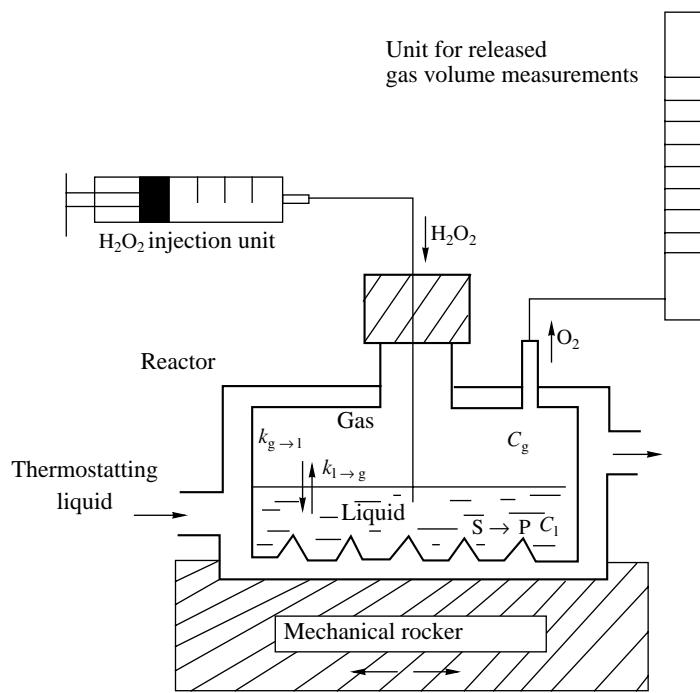
The steady-state kinetics of the side reaction of oxidant decomposition can also be studied for determining the kinetic parameters of the reaction (order of reaction and activation energy) from the dependence of the rate of oxidant decomposition on the steady-state concentration of the oxidant.

The experimental setup developed for these studies (figure) consists of a mechanical rocker (oscillation frequency of 500–700 Hz), a volumetric unit, a thermostat, and a system for the continuous injection of an oxidant.

The following terms and symbols will be used in calculations:

t is time, h;

V is the total reactor volume, ml;



Schematic diagram of the setup for kinetic studies with the continuous injection of hydrogen peroxide.

$V_g(t)$ and $V_l(t)$ are the volumes of gas and liquid phases, respectively, ml;

$\lambda(t) = V_g(t)/V_l(t)$ is the ratio between the volumes of gas and liquid phases at the point in time t ;

$N(t)$ is the total number of moles of substrate S in the gas and liquid phases;

$N_g(t)$ and $N_l(t)$ are the numbers of substrate moles in the gas and liquid phases, respectively;

$C_g(t)$ and $C_l(t)$ are the substrate concentrations in the gas and liquid phases, respectively, mol/l;

$\alpha = C_g(t)/C_l(t)$ is the ratio between equilibrium gas concentrations in the gas and liquid phases;

$k_{g \rightarrow 1}$ and $k_{1 \rightarrow g}$ are the rate constants of mass transfer of the substrate from a gas to a liquid and from a liquid to a gas, respectively;

W is the volumetric rate of oxygen release in the system, ml/h;

ω is the volumetric rate of supply of the hydrogen peroxide solution, ml/h;

k is the reaction rate constant of substrate oxidation, $\text{mol}^{n-1}\text{l}^{1-n}\text{h}^{-1}$;

n is the order of oxidation reaction with respect to the substrate.

Let us find a procedure for calculating the reaction rate constant of oxidation of gaseous substrate S from values measured in the described system (figure). The following processes occur in the system depicted in the figure:

(1) The removal of substrate S and a standard substance from a gas phase with the flow of released oxy-

gen. A decrease in the total amount of a substance in the gas phase due to this process is described by the equation

$$-\frac{dN_g(t)}{dt} = \frac{(W + \omega)N_g(t)}{V_g(t)}. \quad (1)$$

(2) A change in the total amount of the substrate or the standard substance in the gas and liquid phases due to mass transfer between them is described by the following set of equations:

$$\begin{cases} \frac{dN_g(t)}{dt} = -k_{g \rightarrow 1}C_g(t) + k_{g \rightarrow 1}C_l(t) \\ \frac{dN_l(t)}{dt} = k_{g \rightarrow 1}C_g(t) - k_{1 \rightarrow g}C_l(t) \\ k_{g \rightarrow 1}\alpha = k_{1 \rightarrow g} \text{ Henry's law.} \end{cases} \quad (2)$$

In this case, the proportionality factor α depends on the temperature, pH, and composition of the solution.

(3) A change in the total amount of substrate S in the liquid phase due to the occurrence of the chemical reaction of S oxidation to products:

$$\frac{dN_l(t)}{dt} = kC_l(t)^nV_l(t). \quad (3)$$

Now, we can easily derive the complete system of differential equations, which describes changes in the

concentration of the substrate or the standard substance in the gas and liquid phases:

$$\begin{cases} \frac{d[C_g(t)V_g(t)]}{dt} = -k_{g \rightarrow l}C_g(t) + k_{l \rightarrow g}C_l(t) - \frac{(W + \omega)N_g(t)}{V_g(t)} \\ \frac{d[C_l(t)V_l(t)]}{dt} = k_{g \rightarrow l}C_g(t) - k_{l \rightarrow g}C_l(t) - kC_l(t)^nV_l(t). \end{cases} \quad (4)$$

We introduce the parameter λ as follows:

$$\lambda(t) = V_g(t)/V_l(t) = \frac{V\lambda(0) - \omega t[1 + \lambda(0)]}{V + \omega t[1 + \lambda(0)]}. \quad (5)$$

Hence, the following relationships can be derived:

$$V_g(t) = \frac{V\lambda(t)}{1 + \lambda(t)}, \quad (6)$$

$$V_l(t) = \frac{V}{1 + \lambda(t)}, \quad (7)$$

$$V(t) = \frac{V_g(t)[1 + \lambda(t)]}{\lambda(t)}. \quad (8)$$

Taking into account Eqs. (5)–(8), set of Eqs. (4) can be used for numerically calculating the rate constant and order of reaction and for testing the statistical confidence of the kinetic equation in use.

As a particular example of the use of the set of Eqs. (4), we consider the following special case of practical importance: the rapid mass transfer of a substrate and a standard substance through a gas–liquid interface and the first-order reaction of substrate oxidation in a liquid. Conditions for the applicability of this approach can be formulated as follows:

$$\begin{cases} k_{g \rightarrow l} \gg k \\ k_{l \rightarrow g} \gg (W + \omega) \end{cases}. \quad (9)$$

Taking into account Eqs. (4)–(8) and assuming that $\frac{C_g(t)}{C_l(t)} = \alpha = \text{const}$ because of rapid mass transfer, we obtain the following differential equations for changes in the experimentally measured concentrations of the substrate C_{g1} (subscript 1) and the standard substance C_{g2} (subscript 2) in the gas phase:

$$\begin{aligned} & -\frac{d}{dt} \left[\ln \frac{C_{g1}(t)(1 + \alpha_1\lambda(t))}{\alpha_1(1 + \lambda(t))} \right] \\ & = \frac{kV + (W + \omega)\alpha_1 + (W + \omega)\alpha_1\lambda(t)}{V[1 + \alpha_1\lambda(t)]}, \end{aligned} \quad (10)$$

$$\begin{aligned} & -\frac{d}{dt} \left[\ln \frac{C_{g2}(t)(1 + \alpha_2\lambda(t))}{\alpha_2(1 + \lambda(t))} \right] \\ & = \frac{(W + \omega)\alpha_2(1 + \lambda(t))}{V(1 + \alpha_2\lambda(t))}. \end{aligned} \quad (11)$$

In the course of an experiment, the concentration ratio between the substrate and the standard substance in the gas phase

$$X(t) = \frac{C_{g1}(t)}{C_{g2}(t)} \quad (12)$$

is measured to the highest accuracy (for example, by gas chromatography).

An equation for $X(t)$ can be easily obtained by subtracting Eq. (11) from Eq. (10):

$$\begin{aligned} & -\frac{d}{dt} \left[\ln \left\{ \frac{\alpha_2(1 + \alpha_1\lambda(t))}{\alpha_1(1 + \alpha_2\lambda(t))} X(t) \right\} \right] = \frac{k}{1 + \alpha_1\lambda(t)} \\ & + \frac{(\alpha_1 - \alpha_2)(W + \omega)(1 + \lambda(t))}{V(1 + \alpha_1\lambda(t))(1 + \alpha_2\lambda(t))}. \end{aligned} \quad (13)$$

It is convenient to introduce the following quantity:

$$\chi(t) = \frac{X(t)}{X(0)}. \quad (14)$$

Now, we obtain the following final equation for k from Eqs. (13) and (14):

$$\begin{aligned} & -\frac{d}{dt} \left[\ln \left\{ \frac{\alpha_2(1 + \alpha_1\lambda(t))}{\alpha_1(1 + \alpha_2\lambda(t))} \chi(t)X(0) \right\} \right] = \frac{k}{1 + \alpha_1\lambda(t)} \\ & + \frac{(\alpha_1 - \alpha_2)(W + \omega)(1 + \lambda(t))}{V(1 + \alpha_1\lambda(t))(1 + \alpha_2\lambda(t))}. \end{aligned} \quad (15)$$

Differential Eq. (15) can be integrated analytically (for example, using the Mathematica 3 package) and solved for the desired rate constant k . We do not give the final analytical expression because it is cumbersome.

EXPERIMENTAL

The use of the proposed procedure is described below.

Determination of Mass-Transfer Rate Constants

For the direct use of Eq. (15), which was derived under the assumption of rapid mass transfer, it is necessary to initially check the validity of conditions (9). For this purpose, the rate constants of mass transfer of the substrate and the standard substance through the interface in the test system should be measured.

To determine the constants of mass transfer, a small amount of the required gas is injected into the gas phase of the reactor containing a reaction solution with no oxidant. In the course of shaking the reactor, the concentration of the gas in the gas phase is determined. Next, with the use of the set of Eqs. (2), the constants of mass transfer and, correspondingly, the equilibrium distribution factor α are determined by the maximum likelihood method.

Kinetic Study of the Oxidation of Gaseous Hydrocarbons

The values of $\chi(t) = X(t)/X(0)$ are experimentally determined for a set of fixed values of t . Here, $X(t)$ is the concentration ratio between the substrate and the standard substance in the gas phase at the point in time t ; $X(0)$ is the above ratio at the point in time taken as a starting point for kinetic calculations. The first point in the kinetic curve is measured some time, which depends on experimental conditions, after the beginning of hydrogen peroxide supply to reach a steady state. Next, χ is plotted as a function of time, and the apparent rate constant and the probable error of its measurement are calculated by the maximum likelihood method using Eq. (11) or (4) (for example, in the Mathematica 3 package).

The calculation error in a function, which depends on a set of parameters, is calculated by a standard method using the equation

$$\sigma^2(f\{a_i\}) = \sum_i \left(\frac{\partial f}{\partial a_i} \right)^2 \sigma_{a_i}^2, \quad (16)$$

where $\{a_i\}$ is the set of parameters and σ_{a_i} is the experimental error in the measurement of the i th parameter.

In our case, the rate constant of substrate oxidation is a function of a number of parameters, which are measured with certain errors:

$$k = f(\alpha_1, \alpha_2, V, \lambda_0, X(t), X(0), W). \quad (17)$$

Hence, we can calculate the probable error σ_k in the determination of the value of k using Eq. (16). The analytical expression for σ_k derived with the use of the Mathematica 3 package is too cumbersome to be cited in a short article.

Kinetic Study of Oxidant Consumption

In the course of hydrogen peroxide injection into the system, a steady-state concentration of hydrogen peroxide is reached in this system. In this case, the rate of decomposition of hydrogen peroxide is equal to the rate of injection; this can be used for studying the reaction kinetics of hydrogen peroxide decomposition.

CONCLUSIONS

The procedure developed was used for studying the oxidation of ethylene by hydrogen peroxide and the reaction of hydrogen peroxide decomposition on the iron oxide $\alpha\text{-Fe}_2\text{O}_3$. The results of these studies were published elsewhere [2, 3].

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