

New Approaches to Simulation of Enzymatic Reactions: Mimetic Catalysis

TM Nagiev

Nagiev Institute of Chemical Problems of National Academy of Sciences

Corresponding author

TM Nagiev, Nagiev Institute of Chemical Problems of National Academy of Sciences, E-mail: tnagiev@azeurotel.com

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Abstract

The examples given below, for instance, methane oxidation to methanol and propylene oxidation to propylene oxide, demonstrate experimental approaches to the study of interfering reaction dynamics and, with the help of the determinant equation, the potential abilities of reaction media are assessed and the type of chemical interference determined.

Keywords: Biosimulator, Monooxygenase, Interference

Experimental: Monooxygenase reaction for synthesizing methanol from methane was studied in the presence of cytochrome P-450 biosimulators, such as ferroporphyrin catalysts with the carriers (Al_2O_3 , NaX, aluminum-chromium-silicate and aluminum-magnesium-silicate). This reaction helped in the detection of the highest catalytic activity for $PPFe^3+OH/$ aluminum-magnesium-silicate, which also displayed the highest catalytic activity for hydroxylation reaction. As shown, optimal hydroxylic activity of the catalyst is displayed in the initial 30 min of its operation (methanol output equals 60 wt.%, selectivity is 97 wt.%).

Results and discussion: Figure 1 shows that kinetic dependence of methanol output on temperature has a maximum

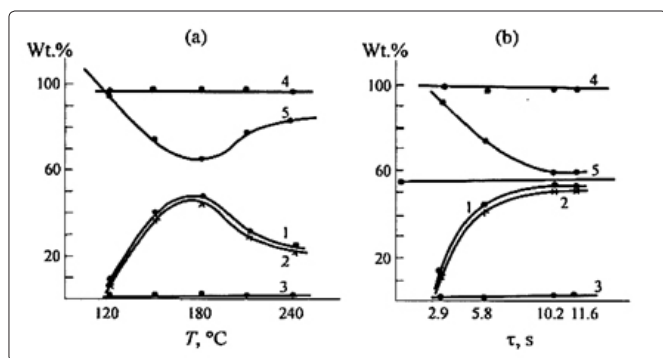
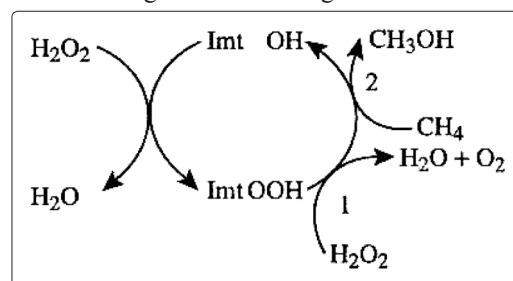


Figure 1: Dependencies of methane hydroxylation outputs on (a) temperature and (b) contact time at 180°C. 1: CH_4 conversion; 2: CH_3OH output; 3: CH_2O and $HCOOH$ outputs; 4: selectivity; 5: O_2 output Ratios: $CH_4:H_2O_2 = 1:1.4$ (a) and $1:1.8$ (b); $VCH_4:VH_2O_2 = 0.8$ ml/h, $[H_2O_2] = 20$ wt.%.

at 180°C, and the curve of molecular oxygen yield has a minimum. In this experiment, methanol yield reaches 46.5 wt.%, which at

methane conversion rises to 48 wt.%. Nontarget products CH_2O and $HCOOH$ in low amounts ($\approx 1.5\%$) and temperature cause no effect on their yield. Comparison of the curves 2 and 5 in Figure 1a in the framework of the ideas discussed above shows their reliable analogy with the theoretical curves [1]. A graphic presentation of chemical interference, shaped as asymptotically approaching curves in another range of the reaction conditions, is plotted in Figure 1b. Comparison of the experimental curves from Figure 1b with the theoretical ones from Figure 1b indicates their adequacy and relates the observable chemical interference to the case above X, i.e. when the CH_4 oxidation rate slightly exceeds the rate of molecular oxygen synthesis.

In the chemical system studied biosimulator catalyzes two interrelated (catalase and mono-oxygenase) reactions, which are synchronized and proceed according to the following mechanisms:



where $ImtOH$ is $PPFe^{3+}OH/AlMgSi$ biosimulator; $ImtOOH$ is $PPFe^{3+}OH/AlMgSi$ intermediating compound: (1) primary catalase reaction and (2) hydroxylation (secondary monooxygenase reaction).

Both reactions (1) and (2) in the scheme proceed via general $PPFe^{3+}OH/AlMgSi$ intermediating compound, which certainly is the transferring agent for the inductive action of the primary reaction to the secondary reaction. The determinant calculated by equation, which allows quantitative identification of an interaction between reactions, equals: $D = 0.48$ [1].

This indicates that reactions (1) and (2) are conjugated, because the value obtained on the determinant scale of chemical interaction falls within the range of chemical conjugation ($D < 1$), because in the current case $\nu = 1$.

The diagrams in Figure 2 illustrate the conjugated type of two reactions: H_2O_2 dissociation and propylene epoxidation by hydrogen peroxide. Actually, the rate decrease of biosimulator catalase activity product (O_2) accumulation is accompanied by the rate increase of epoxidation product synthesis, and these processes interfere via general highly active intermediating compound: per-FTPhFe³⁺OOH/ Al_2O_3 .

However, presenting the interference picture via a diagram has several principal disadvantages: 1. diagrams do not show how coherence is implemented; 2. phase shifts may not be shown; 3. maxima and minima in accumulation of products of both reactions and 4. the absence of asymptotic curves.

The advantage of the diagrams is that they are highly illustrative of chemical conjugation between current reactions. Thus, diagrams help in demonstrating one of the aspects of chemical interference associated with conjugation of the processes.

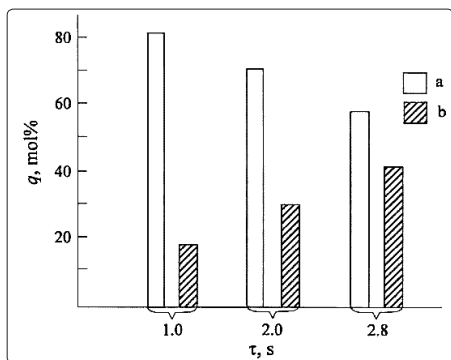


Figure 2: Hydrogen peroxide consumption (q) in catalase (a) and monoxygenase (b) reactions with time of contact; $T = 200^\circ\text{C}$, $C_3H_6:H_2O_2 = 1:1.2$ (mol).

Let us consider the experimental data shown in Figure 3a and b, obtained at homogeneous gas-phase oxidation of methane (or natural gas) by hydrogen peroxide to methanol under pressure. The increase in contact time to 0.95 s (Figure 3a) gives a maximum of methanol output and a minimum of oxygen output. A further increase in the contact time reduces methanol output, whereas molecular oxygen output increases. A similar kinetic regularity is observed in experiments with variable pressure (Figure 3b).

Thus, comparison of the curves of molecular oxygen accumulation and CH_4 consumption (or CH_3OH accumulation) shows that the maximum of CH_4 transformation corresponds to the minimum of O_2 accumulation.

Chemical interference is clearly displayed owing to almost 100% selectivity of reactions: increased O_2 synthesis induces a simultaneous decrease of CH_4 transformation to CH_3OH and vice versa.

As the curves in Figure 3a and b are considered from positions of coherence and possible phase shift, note that the particular reaction mixture differs from the mixtures considered above by relatively low

(about 20wt.%) CH_4 substrate conversion, although H_2O_2 dissociates almost completely. This circumstance must be taken into account in the frame work of the approach to such a case described above.

Experimental detection of chemical interference determinant by the following equation:

$$D = \nu \left(\frac{r_1}{r_{CH_4}} + \frac{r_2}{r_{CH_4}} \right)^{-1}$$

where $r_{H_2O_2}$ and r_{CH_4} are actor (H_2O_2), inducer (H_2O_2) and acceptor (CH_4) consumption rates, respectively; ν is the stoichiometric coefficient equal to 1 for the current conditions of minimal O_2 and maximal CH_3OH outputs, gave $D = 0.18$. On the chemical interference scale in Figure 2.1, this value falls within the range for conjugated reactions. It quantitatively characterizes the inductive action of H_2O_2 on CH_4 oxidation and indicates the presence of high potential abilities to increase the induction effect of the system studied (theoretically, in the current case, D may increase to 1 or will tend to approach at least the 50% level) [1]. There are physicochemical experimental techniques that allow manipulation of conjugating reaction rates. On the other hand, not applying the method of stationary concentrations, the determinant equation [1] gives an opportunity of analyzing the kinetics of complex reactions with insignificantly studied mechanisms. For these two reactions the conjugation mechanism is:

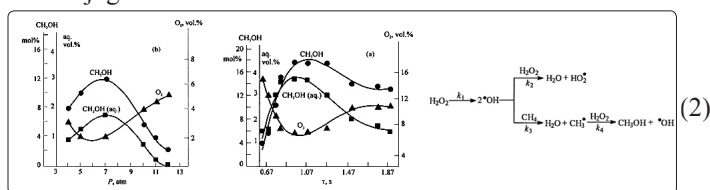


Figure 3: The dependence of methanol output on the contact time (a) and pressure (b); $T = 400^\circ\text{C}$, $[H_2O_2] = 30$ wt.% (a) $p = 7$ atm; $V_{CH_4} = 31.41/h$; $V_{H_2O_2} = 0.18$ l/h; $CH_4:H_2O_2 = 1:1.4$ (mol) and (b) $V_{H_2O_2} = 0.18$ l/h;

$V_{CH_4} = 62.4$ l/h; $CH_4:H_2O_2 = 1:0.4$ (mol).

As follows from the determinant

$$r_{acc}(CH_4) = \frac{D}{\nu} (r_{A_1} + r_{A_2}) \quad r_{CH_4} = \frac{D}{\nu} (k_2[H_2O_2] + k_3[CH_4])[OH] \quad (3)$$

Using experimentally obtained values of r_{CH_4} and D , the appropriate kinetic calculations were carried out. Therefore, equation (3) adequately describes the kinetics of interfering reaction (2).

References

1. TM Nagiev (2007) Coherent Synchronized Oxidation Reactions by Hydrogen Peroxide. Elsevier. Amsterdam 325.

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