

# Supporting Information: The Effect of Metals of the 2nd and 12th Groups on the Productivity and Selectivity of Cumene Oxidation—The First Stage of the Technological Chain for the Production of Polymer Composites

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**S1. The mathematical model of the kinetics for cumene oxidation and cumene hydroperoxide decomposition in the presence of Ma, Ca, Sr, Ba, Zn, Cd of Hg 2-ethylhexanoate as a catalyst**

$$\begin{aligned} \frac{d[RH]}{dt} = & -k_1[RH][Cat] + k_1'[RH \cdot Cat] - k_5[RH][O_2] - k_{12}[RH][ROO^\bullet] - \\ & -k_{14}[RH][RO^\bullet] - k_{16}[RH][^\bullet OH] - k_{23}[CH_3OO^\bullet][RH], \\ \frac{d[Cat]}{dt} = & -k_1[RH][Cat] + k_1'[RH \cdot Cat] - k_2[ROOH][Cat] + k_2'[ROOH \cdot Cat] - \\ & -k_3[ROH][Cat] + k_3'[ROH \cdot Cat] - k_4[HC(O)H][Cat] + k_6[RH \cdot Cat][O_2] + \\ & +k_8[ROOH \cdot Cat] + 2k_{10}[ROOH \cdot Cat]^2 + k_{13}[RH \cdot Cat][ROO^\bullet] + \\ & +k_{15}[RH \cdot Cat][RO^\bullet] + k_{17}[RH \cdot Cat][^\bullet OH] + k_{19}[ROOH \cdot Cat][RO^\bullet] + \\ & +k_{24}[CH_3OO^\bullet][RH \cdot Cat] + k_{35}[ROH \cdot Cat] + k_{36}[HC(O)H \cdot Cat][O_2]^{0.5} + \\ & +k_{38}[ROOH \cdot Cat] + k_{40}[ROOH \cdot Cat][ROH] - k_{44}[Cat] + k_{45}[ROH \cdot Cat] + \\ & +k_{46}[ROOH \cdot Cat][C_6H_5C(CH_3)=CH_2] - k_{47}[C_6H_5OH]^2[Cat], \\ \frac{d[RH \cdot Cat]}{dt} = & k_1[RH][Cat] - k_1'[RH \cdot Cat] - k_6[RH \cdot Cat][O_2] - \end{aligned}$$

$$\begin{aligned}
& -k_{13}[\text{RH} \cdot \text{Cat}][\text{ROO}^\bullet] - k_{15}[\text{RH} \cdot \text{Cat}][\text{RO}^\bullet] - k_{17}[\text{RH} \cdot \text{Cat}][^\bullet\text{OH}] - \\
& -k_{24}[\text{CH}_3\text{OO}^\bullet][\text{RH} \cdot \text{Cat}], \\
\frac{d[\text{ROOH}]}{dt} = & -k_2[\text{ROOH}][\text{Cat}] + k_{21}[\text{ROOH} \cdot \text{Cat}] - k_7[\text{ROOH}] - 2k_9[\text{ROOH}]^2 + \\
& + k_{12}[\text{RH}][\text{ROO}^\bullet] + k_{13}[\text{RH} \cdot \text{Cat}][\text{ROO}^\bullet] - k_{18}[\text{ROOH}][\text{RO}^\bullet] + \\
& + k_{25}[\text{C}_6\text{H}_5\text{OH}][\text{ROO}^\bullet] + k_{33}[\text{R}^\bullet][^\bullet\text{OOH}] - k_{37}[\text{ROOH}] - k_{39}[\text{ROOH}][\text{ROH}] - \\
& - k_{41}[\text{ROOH}][\text{HCOOH}] + k_{41'}[\text{ROOH} \cdot \text{HCOOH}], \\
\frac{d[\text{ROOH} \cdot \text{Cat}]}{dt} = & k_2[\text{ROOH}][\text{Cat}] - k_{21}[\text{ROOH} \cdot \text{Cat}] - k_8[\text{ROOH} \cdot \text{Cat}] - \\
& - 2k_{10}[\text{ROOH} \cdot \text{Cat}]^2 - k_{19}[\text{ROOH} \cdot \text{Cat}][\text{RO}^\bullet] - k_{38}[\text{ROOH} \cdot \text{Cat}] - \\
& - k_{40}[\text{ROOH} \cdot \text{Cat}][\text{ROH}] - k_{46}[\text{ROOH} \cdot \text{Cat}][\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2], \\
\frac{d[\text{ROH}]}{dt} = & -k_3[\text{ROH}][\text{Cat}] + k_3'[\text{ROH} \cdot \text{Cat}] + k_{14}[\text{RH}][\text{RO}^\bullet] + k_{15}[\text{RH} \cdot \text{Cat}][\text{RO}^\bullet] + \\
& + k_{18}[\text{ROOH}][\text{RO}^\bullet] + k_{19}[\text{ROOH} \cdot \text{Cat}][\text{RO}^\bullet] + k_{30}[\text{CH}_3\text{OO}^\bullet][\text{ROO}^\bullet] - k_{34}[\text{ROH}] - \\
& - k_{39}[\text{ROOH}][\text{ROH}] + 2k_{39}[\text{ROOH}][\text{ROH}] - k_{40}[\text{ROOH} \cdot \text{Cat}][\text{ROH}] + \\
& + 2k_{40}[\text{ROOH} \cdot \text{Cat}][\text{ROH}] + k_{46}[\text{ROOH} \cdot \text{Cat}][\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2], \\
\frac{d[\text{ROH} \cdot \text{Cat}]}{dt} = & k_3[\text{ROH}][\text{Cat}] - k_3'[\text{ROH} \cdot \text{Cat}] - k_{35}[\text{ROH} \cdot \text{Cat}] - k_{45}[\text{ROH} \cdot \text{Cat}], \\
\frac{d[\text{HC(O)H}]}{dt} = & -k_4[\text{HC(O)H}][\text{Cat}] + k_{30}[\text{CH}_3\text{OO}^\bullet][\text{ROO}^\bullet] + \\
& + k_{43}[\text{C}_6\text{H}_5\text{CH}_3\text{C}=\text{CH}_2][\text{O}_2], \\
\frac{d[\text{HC(O)H} \cdot \text{Cat}]}{dt} = & k_4[\text{HC(O)H}][\text{Cat}] - k_{36}[\text{HC(O)H} \cdot \text{Cat}][\text{O}_2]^{0.5}, \\
\frac{d[\text{O}_2]}{dt} = & -k_5[\text{RH}][\text{O}_2] - k_6[\text{RH} \cdot \text{Cat}][\text{O}_2] - k_{11}[\text{R}^\bullet][\text{O}_2] + k_{21}[\text{ROO}^\bullet]^2 - \\
& - k_{22}[\text{CH}_3^\bullet][\text{O}_2] + k_{29}[\text{ROO}^\bullet]^2 + k_{30}[\text{CH}_3\text{OO}^\bullet][\text{ROO}^\bullet] + k_{31}[\text{C}_6\text{H}_5\text{O}^\bullet][\text{ROO}^\bullet] + \\
& + 0.5k_{32}[\text{C}_6\text{H}_5\text{O}^\bullet][\text{ROO}^\bullet] - 0.5k_{36}[\text{HC(O)H} \cdot \text{Cat}][\text{O}_2]^{0.5} + 0.5k_{39}[\text{ROOH}][\text{ROH}] +
\end{aligned}$$

$$+0.5k_{40}[\text{ROOH} \cdot \text{Cat}][\text{ROH}] - k_{43}[\text{C}_6\text{H}_5\text{CH}_3\text{C}=\text{CH}_2][\text{O}_2] + \text{M},$$

$$\begin{aligned} \frac{d[\text{R}^\bullet]}{dt} = & k_5[\text{RH}][\text{O}_2] + k_6[\text{RH} \cdot \text{Cat}][\text{O}_2] - k_{11}[\text{R}^\bullet][\text{O}_2] + k_{12}[\text{RH}][\text{ROO}^\bullet] + \\ & + k_{13}[\text{RH} \cdot \text{Cat}][\text{ROO}^\bullet] + k_{14}[\text{RH}][\text{RO}^\bullet] + k_{15}[\text{RH} \cdot \text{Cat}][\text{RO}^\bullet] + k_{16}[\text{RH}][^\bullet\text{OH}] + \\ & + k_{17}[\text{RH} \cdot \text{Cat}][^\bullet\text{OH}] + k_{23}[\text{CH}_3\text{OO}^\bullet][\text{RH}] + k_{24}[\text{CH}_3\text{OO}^\bullet][\text{RH} \cdot \text{Cat}] - \\ & - 2k_{26}[\text{R}^\bullet]^2 - k_{27}[\text{R}^\bullet][\text{ROO}^\bullet] - k_{33}[\text{R}^\bullet][^\bullet\text{OOH}], \end{aligned}$$

$$\frac{d[^\bullet\text{OOH}]}{dt} = k_5[\text{RH}][\text{O}_2] + k_6[\text{RH} \cdot \text{Cat}][\text{O}_2] - k_{33}[\text{R}^\bullet][^\bullet\text{OOH}],$$

$$\begin{aligned} \frac{d[\text{RO}^\bullet]}{dt} = & k_7[\text{ROOH}] + k_8[\text{ROOH} \cdot \text{Cat}] + k_9[\text{ROOH}]^2 + k_{10}[\text{ROOH} \cdot \text{Cat}]^2 - \\ & - k_{14}[\text{RH}][\text{RO}^\bullet] - k_{15}[\text{RH} \cdot \text{Cat}][\text{RO}^\bullet] - k_{18}[\text{ROOH}][\text{RO}^\bullet] - \\ & - k_{19}[\text{ROOH} \cdot \text{Cat}][\text{RO}^\bullet] - k_{20}[\text{RO}^\bullet] + 2k_{21}[\text{ROO}^\bullet]^2, \end{aligned}$$

$$\begin{aligned} \frac{d[^\bullet\text{OH}]}{dt} = & k_7[\text{ROOH}] + k_8[\text{ROOH} \cdot \text{Cat}] - k_{16}[\text{RH}][^\bullet\text{OH}] - k_{17}[\text{RH} \cdot \text{Cat}][^\bullet\text{OH}] - \\ & - k_{28}[\text{CH}_3^\bullet][^\bullet\text{OH}], \end{aligned}$$

$$\begin{aligned} \frac{d[\text{ROO}^\bullet]}{dt} = & k_9[\text{ROOH}]^2 + k_{10}[\text{ROOH} \cdot \text{Cat}]^2 + k_{11}[\text{R}^\bullet][\text{O}_2] - \\ & - k_{12}[\text{RH}][\text{ROO}^\bullet] - k_{13}[\text{RH} \cdot \text{Cat}][\text{ROO}^\bullet] + k_{18}[\text{ROOH}][\text{RO}^\bullet] + \\ & + k_{19}[\text{ROOH} \cdot \text{Cat}][\text{RO}^\bullet] - 2k_{21}[\text{ROO}^\bullet]^2 - k_{25}[\text{C}_6\text{H}_5\text{OH}][\text{ROO}^\bullet] + \\ & - k_{27}[\text{R}^\bullet][\text{ROO}^\bullet] - 2k_{29}[\text{ROO}^\bullet]^2 - k_{30}[\text{CH}_3\text{OO}^\bullet][\text{ROO}^\bullet] - \\ & - k_{31}[\text{C}_6\text{H}_5\text{O}^\bullet][\text{ROO}^\bullet] - k_{32}[\text{C}_6\text{H}_5\text{O}^\bullet][\text{ROO}^\bullet], \end{aligned}$$

$$\begin{aligned} \frac{d[\text{H}_2\text{O}]}{dt} = & k_9[\text{ROOH}]^2 + k_{10}[\text{ROOH} \cdot \text{Cat}]^2 + k_{16}[\text{RH}][^\bullet\text{OH}] + \\ & + k_{17}[\text{RH} \cdot \text{Cat}][^\bullet\text{OH}] + k_{34}[\text{ROH}] + k_{35}[\text{ROH} \cdot \text{Cat}] + \\ & + k_{40}[\text{C}_6\text{H}_5\text{CH}_3\text{C}=\text{CH}_2][\text{O}_2], \end{aligned}$$

$$\frac{d[C_6H_5C(O)CH_3]}{dt} = k_{20}[RO^\bullet] + k_{43}[C_6H_5CH_3C=CH_2][O_2] + k_{45}[ROH \cdot Cat],$$

$$\frac{d[CH_3^\bullet]}{dt} = k_{20}[RO^\bullet] - k_{22}[CH_3^\bullet][O_2] - k_{28}[CH_3^\bullet][^\bullet OH],$$

$$\frac{d[CH_3OO^\bullet]}{dt} = k_{22}[CH_3^\bullet][O_2] - k_{23}[CH_3OO^\bullet][RH] -$$

$$-k_{24}[CH_3OO^\bullet][RH \cdot Cat] - k_{30}[CH_3OO^\bullet][ROO^\bullet],$$

$$\frac{d[CH_3OOH]}{dt} = k_{23}[CH_3OO^\bullet][RH] + k_{24}[CH_3OO^\bullet][RH \cdot Cat],$$

$$\frac{d[C_6H_5OH]}{dt} = -k_{25}[C_6H_5OH][ROO^\bullet] + k_{31}[C_6H_5O^\bullet][ROO^\bullet] + k_{37}[ROOH] +$$

$$+k_{38}[ROOH \cdot Cat] + k_{42}[ROOH \cdot HCOOH] - 2k_{47}[C_6H_5OH]^2[Cat],$$

$$\frac{d[C_6H_5O^\bullet]}{dt} = k_{25}[C_6H_5OH][ROO^\bullet] - k_{31}[C_6H_5O^\bullet][ROO^\bullet] -$$

$$-k_{32}[C_6H_5O^\bullet][ROO^\bullet],$$

$$\frac{d[RR]}{dt} = k_{26}[R^\bullet]^2,$$

$$\frac{d[ROOR]}{dt} = k_{27}[R^\bullet][ROO^\bullet] + k_{29}[ROO^\bullet]^2,$$

$$\frac{d[CH_3OH]}{dt} = k_{28}[CH_3^\bullet][^\bullet OH],$$

$$\frac{d[C_6H_5C(CH_3)=CH_2]}{dt} = k_{31}[C_6H_5O^\bullet][ROO^\bullet] + k_{34}[ROH] + k_{35}[ROH \cdot Cat] -$$

$$-k_{43}[C_6H_5C(CH_3)=CH_2][O_2] - k_{46}[ROOH \cdot Cat][C_6H_5C(CH_3)=CH_2],$$

$$\frac{d[C_6H_5OOR]}{dt} = k_{32}[C_6H_5O^\bullet][ROO^\bullet],$$

$$\frac{d[HCOOH]}{dt} = k_{36}[HC(O)H \cdot Cat][O_2]^{0.5} - k_{41}[ROOH][HCOOH] +$$

$$+k_{41}'[ROOH \cdot HCOOH] + k_{42}[ROOH \cdot HCOOH],$$

$$\frac{d[\text{CH}_3\text{C}(\text{O})\text{CH}_3]}{dt} = k_{37}[\text{ROOH}] + k_{38}[\text{ROOH} \cdot \text{Cat}] + k_{42}[\text{ROOH} \cdot \text{HCOOH}],$$

$$\frac{d[\text{ROOH} \cdot \text{HCOOH}]}{dt} = k_{41}[\text{ROOH}][\text{HCOOH}] - k_{41}'[\text{ROOH} \cdot \text{HCOOH}] -$$

$$-k_{42}[\text{ROOH} \cdot \text{HCOOH}],$$

$$\frac{d[\text{Cat}']}{dt} = k_{44}[\text{Cat}],$$

$$\frac{d[\text{CH}_4]}{dt} = k_{45}[\text{ROH} \cdot \text{Cat}],$$

$$\frac{d[\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{O})(\text{CH}_2)]}{dt} = k_{46}[\text{ROOH} \cdot \text{Cat}][\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2]$$

$$\frac{d[(\text{C}_6\text{H}_5\text{O})_2\text{Me}]}{dt} = k_{47}[\text{C}_6\text{H}_5\text{OH}]^2[\text{Cat}],$$

$$\frac{d[\text{H}_3\text{C}(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COOH}]}{dt} = k_{47}[\text{C}_6\text{H}_5\text{OH}]^2[\text{Cat}].$$

In this model, the equation of changing the concentration of the oxygen dissolved in the reaction mixture was written as follows:

$$\frac{d[\text{O}_2]}{dt} = M + X,$$

where  $[\text{O}_2]$  is the oxygen concentration in the reaction mixture,  $\text{kmol/m}^3$ ;  $X$  is the oxygen concentration change rate in the reaction mixture due to chemical reaction,  $\text{kmol}/(\text{m}^3 \cdot \text{s})$ ;  $M$  is the oxygen concentration change rate due to its dissolution in the reaction mixture (that is, due to oxygen mass transfer from the gas phase to the liquid phase),  $\text{kmol}/(\text{m}^3 \cdot \text{s})$ . The formula for calculating  $M$  was taken from work [Kh.E. Kharlampidi, K.A. Tereshchenko, T.Sh. Nurmurodov, D.A. Shiyan, N.P. Miroshkin, N.N. Ziyatdinov, A.S. Ziganshina, N.M. Nurullina, S.L. Khursan, N.V. Ulitin, Chem. Eng. J. 392 (2020) 123811, <https://doi.org/10.1016/j.cej.2019.123811>]:

$$M = \frac{G([\text{O}_2^g] - m[\text{O}_2])(1 - e^{-\frac{K_y U}{G}})}{W},$$

where  $G$  is a volume flow rate of the nitrogen-oxygen mixture,  $\text{m}^3/\text{s}$ ;  $[\text{O}_2^g]$  is an oxygen concentration in nitrogen-oxygen mixture at the inlet of the reactor,  $\text{kmol/m}^3$ ;  $[\text{O}_2]$  is an oxygen concentration in the reaction mixture,  $\text{kmol/m}^3$ ;  $m$  is Henry's solubility coefficient which was calculated in UniSim Design software package [Industrial automation and control solutions from Honeywell, <https://www.honeywellprocess.com> 2022 (accessed 9 November 2022)], it shows the ratio of the oxygen concentration in the nitrogen-oxygen mixture versus the oxygen concentration in the reaction mixture (the rates of oxygen transfer from the nitrogen-oxygen mixture to the reaction mixture and the reverse are equal to each other);  $K_y$  is an oxygen overall mass

transfer coefficient from the nitrogen-oxygen mixture to the reaction mixture, m/s;  $U$  is a total surface area of the oxygen mass transfer from the nitrogen-oxygen mixture to the reaction mixture, m<sup>2</sup>;  $W$  is a reactor volume, m<sup>3</sup>.

The model is applicable to describe the kinetics of cumene oxidation and cumene hydroperoxide decomposition at  $M \neq 0$  (if the processes running in the continuous stirred-tank reactor (CSTR) for liquid phase and plug-flow reactor for gas phase are described) and it is applicable to describe the kinetics of cumene hydroperoxide decomposition at  $M = 0$  (if the processes running in the continuous stirred-tank reactor (CSTR) are described).

In order to determine the values of the pre-exponential factors  $A$  and the activation energies  $E$  in the Arrhenius dependences of the rate coefficients, the inverse kinetic problem was solved. The inverse kinetic problem is the one to determine such model parameters for which the discrepancy is minimal between the data calculated using the model and the experimental data. The solution of the inverse problem was implemented in the Wolfram Mathematica software package. For the numerical solution of the resulting system of differential equations, the BDF method of the 5th order was used, which refers to implicit methods, so it is well suited for solving rigid systems of differential equations. This method calculated the derivatives of the functions  $[C]_r$  (in our case, such functions are the concentrations of species) at a certain time ( $r$  is the current number of the time step), using information about the values of the functions at previous points in time:

$$h_r \left( \frac{[C]_r}{dt} \right)_{t=t_r} = \sum_{a=1}^q \alpha_{r,a} [C]_{r-a}$$

where  $q$  is the order of the method (in our case,  $q = 5$ );  $\alpha_{r,a}$  is a coefficient depending on  $q$  and the size of the completed step  $h_r$ ;  $a = 1, 2, \dots, q$  is the index. As a result, the calculation was reduced to solve a system of equations of the following form:

$$\Phi \left( t_r, [C]_r, \frac{1}{h_r}, \sum_{a=1}^q \alpha_{r,a} [C]_{r-a} \right) = 0$$

This system was solved by the Newton method using an approximation to the Jacobi matrix:

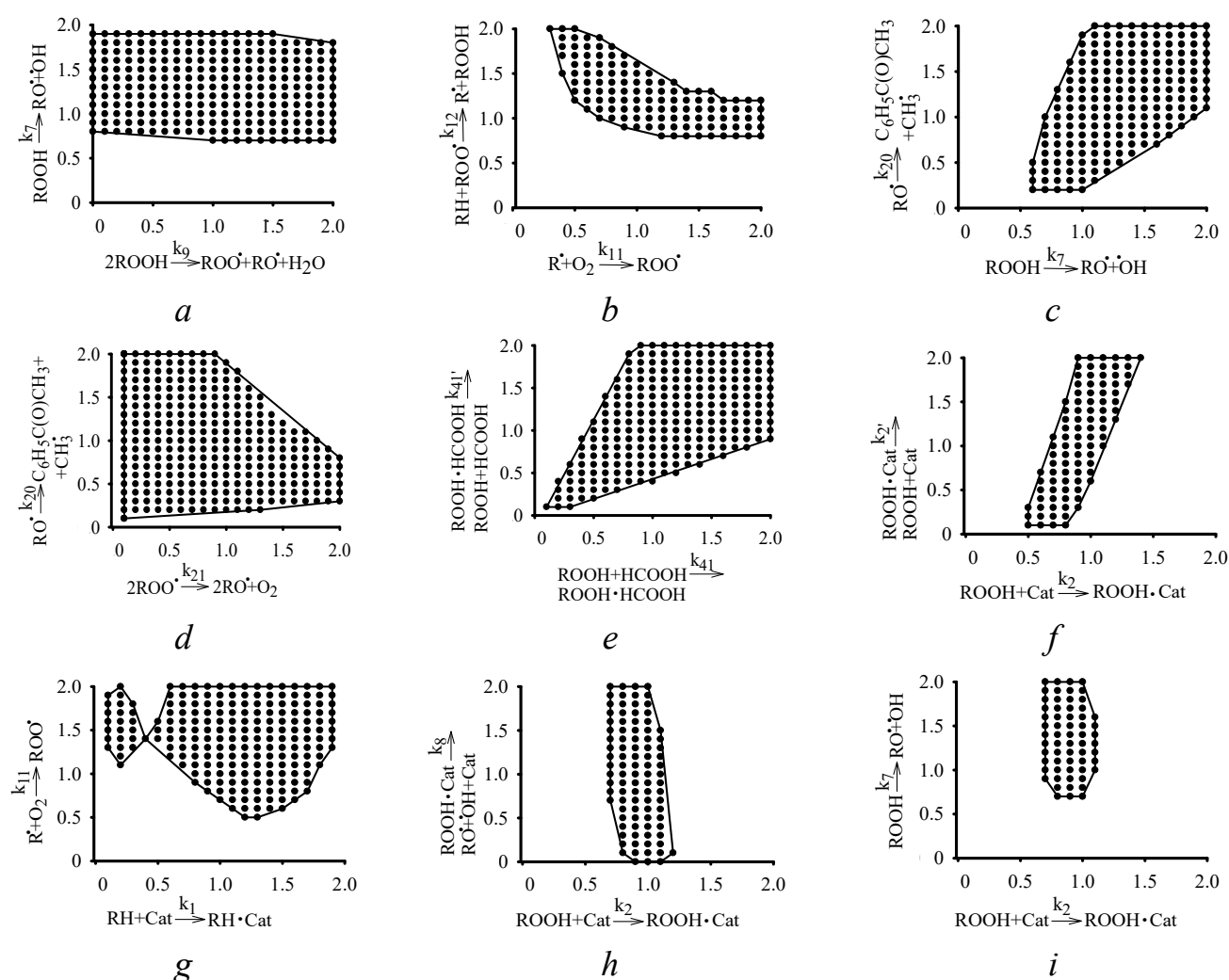
$$J = \frac{d\Phi}{d[C]_r} + c_r \frac{d\Phi}{d \left( \frac{d[C]_r}{dt} \right)},$$

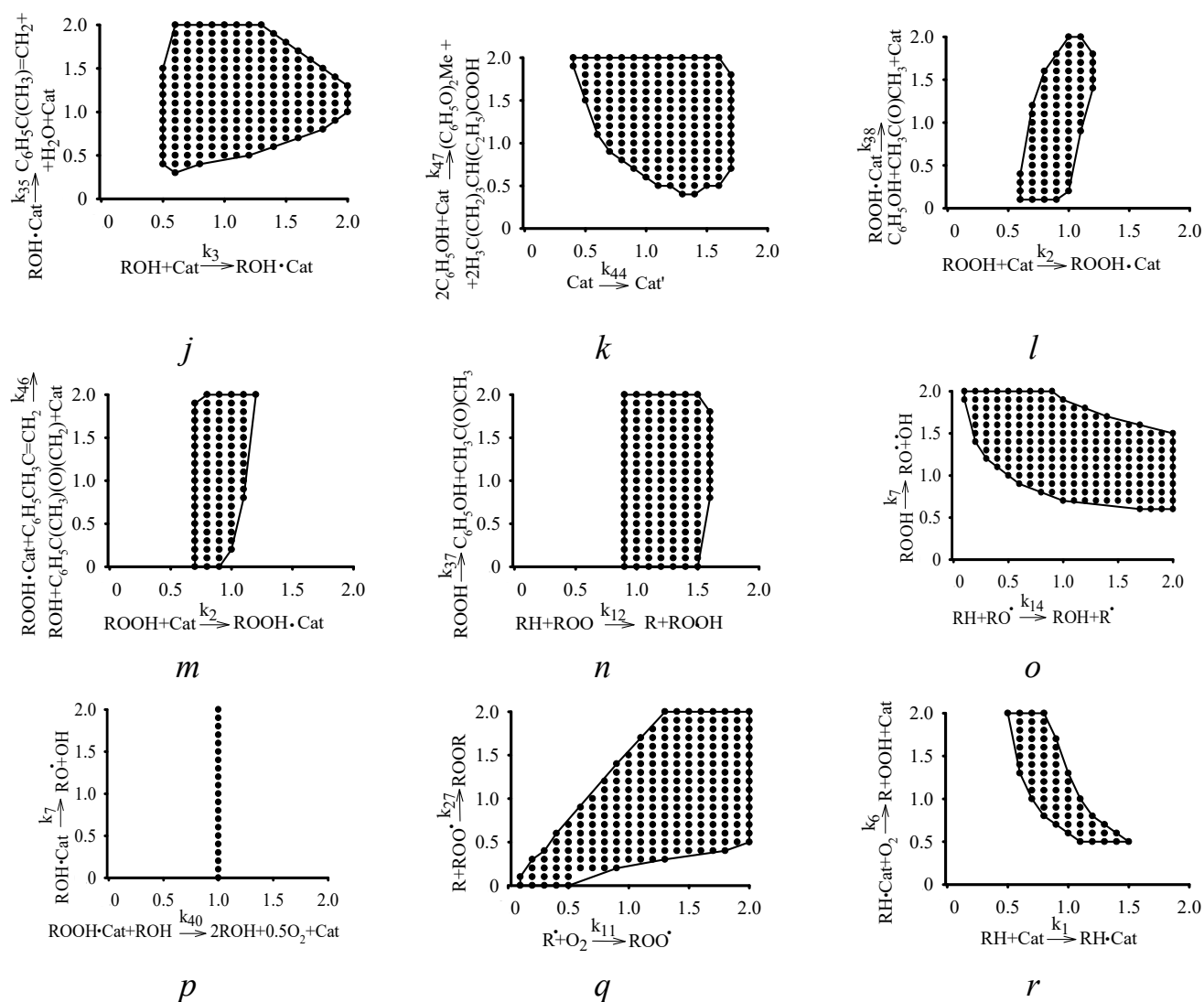
where  $\alpha_{r,0}$  is the value of  $\alpha_{r,a}$  at  $a = 0$ .

## S2. Two-dimensional uncertainty regions of significant rate coefficients of elementary reactions of cumene oxidation and cumene hydroperoxide decomposition in the presence of Mg 2-ethylhexanoate as a catalyst

The experimental data are described by the kinetic model within the average relative error of the experiment (25%). This condition is satisfied by the whole ranges of coefficients values, which are called areas of uncertainty. To establish the areas of uncertainty, the data calculated by the kinetic model were compared with the experimental data shown in Fig. 1 and in Table. 4 in the main text of the

article. On the axes of Fig. 1A, not the absolute values of the pre-exponential factors  $A$ , but the relative ones are shown. The relative value of the pre-exponential factor  $A$ , equal to 1, means that the pre-exponential factor  $A$  has taken the value shown in Table 2 in the main text of the article. If the relative value of the pre-exponential factor  $A$  is not equal to 1, then similar calculations were carried out taking into account that the pre-exponential factor  $A$  is equal to the value from Table 2 of the main text of the article, multiplied by the relative value of the pre-exponential factor  $A$ . The shape of the two-dimensional uncertainty regions of the pre-exponential factors  $A$  shows a correlation between them. For instance, the area of uncertainty shown in Fig. 1A, *e*, corresponds to the case when the calculation according to the kinetic model is affected by the ratio  $A_{41}/A_{41'}$ . The area of uncertainty shown in Fig. 1A, *b*, corresponds to the case when the calculation according to the kinetic model is affected by the ratio  $A_{12}/A_{11}$ .





**Figure S1.** Two-dimensional uncertainty regions of the considered pairs of significant reaction rate coefficients