KINETICS OF FORMATION OF PEROXYFORMIC ACID

Vladimir MOSOVSKY, Zuzana CVENGROSOVA, Alexander KASZONYI[1],
Milan KRALIK[2] and Milan HRONEC

Department of Organic Technology, Slovak Technical University, 812 37 Bratislava,
Slovak Republic; e-mail: [1] kaszonyi@checdek.chtf.stuba.sk, [2] kralik@checdek.chtf.stuba.sk

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Oxidation kinetics of formic acid with aqueous hydrogen peroxide (30–70%) has been studied at 45 °C with 0–0.1 M H_2SO_4 as a catalyst. A kinetic model has been suggested which satisfactorily describes the oxidation process of formic acid to peroxyformic acid.

Key words: Peroxyformic acid; Hydrogen peroxide; Kinetics; Oxidation.

Aliphatic peroxyacids are obtained by oxidation of the corresponding carboxylic acids with aqueous hydrogen peroxide. The reaction takes place at 20–70 °C in the presence of mineral acids such as H_2SO_4, H_3PO_4 or sulfonated styrene–divinylbenzene copolymers[1–4].

$$\mathrm{RCOOH} + \mathrm{H_2O_2} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{RCOOOH} + \mathrm{H_2O} \qquad (A)$$

It is presumed[5] that the rate-limiting step consists in a nucleophilic reaction of the $RC^+(OH)_2$ or $RC^+(OH)(OOH)$ species with the H_2O_2 or H_2O reagents, respectively.

The processes usually are continuous and the peroxyacid formed is either separated from the reaction mixture by extraction with organic solvents[6–8] or used directly as an oxidant in the form of the peroxyacid–acid mixture.

The aim of the present work was to study the oxidation kinetics and hence suggest a model describing the oxidation of formic acid into peroxyformic acid.

EXPERIMENTAL

Reagents

The solutions of hydrogen peroxide with concentrations from 32 to 70 wt.% were prepared by evaporating water from the commercial H_2O_2 (32 wt.%) from a water bath. The commercial formic acid (99%) was used without purification.

Apparatus

The kinetics of formation of peroxyformic acid was studied in a glass through-flow stirred reactor of 40 cm^3 volume. Hydrogen peroxide and a mixture of HCOOH and H_2SO_4 were dosed into the reactor by means of peristaltic pumps. The inlets of H_2O_2 and HCOOH–H_2SO_4 mixture were placed near the stirrer axis. The reactor was located in a thermostat with water bath. The reaction mixture left the reactor by overflow. All the components of the apparatus in direct contact with the reaction mixture were made of glass and Teflon. After reaching the required temperature and putting the whole apparatus into operation, the reactants started to be dosed into the reactor. After reaching the steady state (ca 3–4 h), samples of the reaction mixture were taken for analyses.

Analysis

The samples of reaction mixture were analyzed for H_2O_2 (cerimetry) and HCO_3H (iodometry)[9]. The values obtained represent the stationary concentrations of hydrogen peroxide and peroxyformic acid in the reaction mixture.

RESULTS AND DISCUSSION

The kinetics of reaction of hydrogen peroxide and formic acid giving peroxyformic acid and water was studied in a through-flow stirred reactor using the 1 : 2.67 molar ratio of the above-mentioned reactants without any solvent at the temperature of 45 °C. The formic acid introduced into the reactor was concentrated (99%, i.e. 26.24 mol dm^{-3}). Using various retention times, we introduced the hydrogen peroxide of the concentrations varying in the interval from 32 to 70 wt.% (10.5 to 29.8 mol dm^{-3}), the catalytic sulfuric acid having the concentrations from 0 to 0.1 mol dm^{-3} in the reaction mixture.

The highest outlet concentrations of peroxyformic acid were obtained with the use of 70 wt.% hydrogen peroxide and at the sulfuric acid concentration of 0.06 mol dm^{-3} in the reaction mixture, the inlet flow-rate of reactants being 0.0228 dm^3 h^{-1}. The results depicted in Figs 1–5 show that the formation of peroxyformic acid is favourably af-

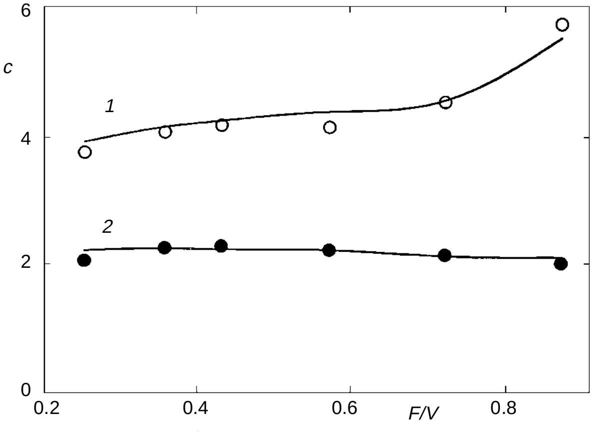

FIG. 1

Dependence of concentration c (mol dm^{-3}) of hydrogen peroxide (*1*) and peroxyformic acid (*2*) on volume rate F/V (h^{-1}). Conditions: 45 °C, inlet concentrations of components: $[H_2O_2]$ = 7.2 mol dm^{-3}, [HCOOH] = 19 mol dm^{-3}, $[H_2SO_4]$ = 0 mol dm^{-3}. Solid line – calculated values (MODEL 1) fected by increasing concentration of both the inlet formic acid and the inlet hydrogen peroxide. At such conditions, minimum amounts of water (water suppresses the formation of peroxyformic acid) are introduced into the system. The results indicate that a lower dosing rate of inlet reactants (i.e. their longer retention time in the reactor) causes increasing decomposition of hydrogen peroxide. The lowering of hydrogen peroxide concentration due to its increased decomposition in the reaction mixture affects unfavourably the formation of peroxyformic acid, hence a lower concentration of peroxyformic acid is observed at the outlet of the reactor. At higher dosing rates of reactants, the reduced reaction time affects the conversion of formic acid but slightly, which is connected with the establishing of equilibrium of formation of peroxyformic acid at the experimental conditions.

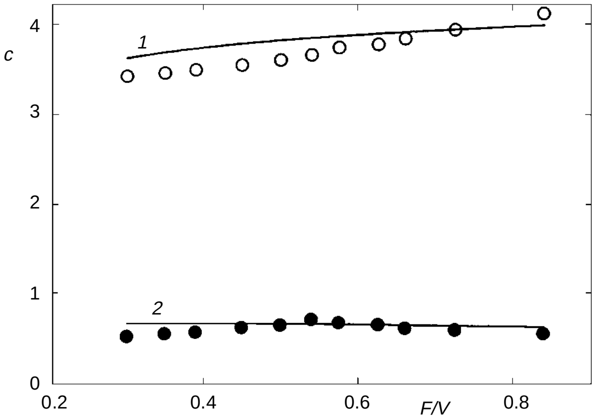

FIG. 2
Dependence of concentration *c* (mol dm^{-3}) of hydrogen peroxide (*1*) and peroxyformic acid (*2*) on volume rate *F/V* (h^{-1}). Conditions: 45 °C, inlet concentrations of components: $[H_2O_2]$ = 4.89 mol dm^{-3}, [HCOOH] = 13.1 mol dm^{-3}, $[H_2SO_4]$ = 0 mol dm^{-3}. Solid line – calculated values (MODEL 1)

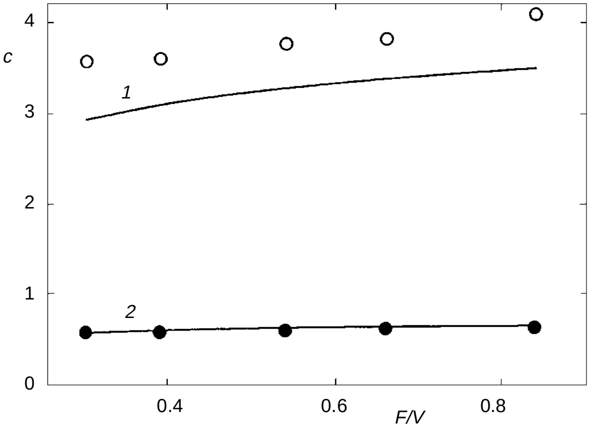

FIG. 3
Dependence of concentration *c* (mol dm^{-3}) of hydrogen peroxide (*1*) and peroxyformic acid (*2*) on volume rate *F/V* (h^{-1}). Conditions: 45 °C, inlet concentrations of components: $[H_2O_2]$ = 4.89 mol dm^{-3}, [HCOOH] = 13.1 mol dm^{-3}, $[H_2SO_4]$ = 0.06 mol dm^{-3}. Solid line – calculated values (MODEL 1)

The presence of sulfuric acid in the reaction mixture increases the overall concentration of hydrogen ions, which in particular affect the decomposition of hydrogen peroxide and peroxyformic acid. As it can be seen from the results the increasing sulfuric acid concentration in the reaction mixture accelerates the decomposition of hydrogen peroxide. The dependence of formation of peroxyformic acid on the sulfuric acid concentration shows an indistinct maximum at the sulfuric acid concentrations from 0.05 to 0.06 mol dm^{-3}.

For kinetic treatment of the experimental data, various models were suggested describing the processes of formation and decomposition of peroxyformic acid and that of decomposition of hydrogen peroxide. All the models presume complete dissociation of sulfuric acid, the total concentration of hydrogen ions involving also the protons com-

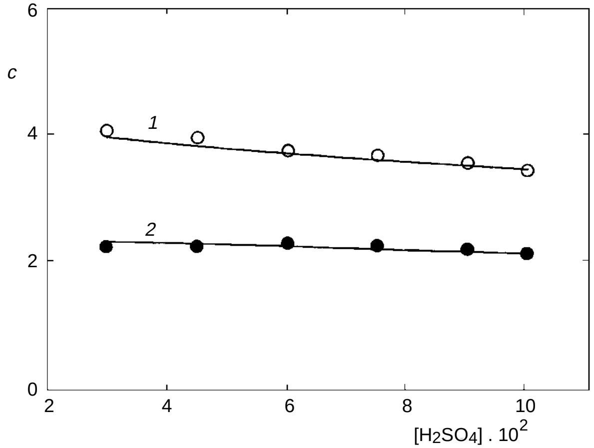

FIG. 4
Dependence of concentration *c* (mol dm^{-3}) of hydrogen peroxide (*1*) and peroxyformic acid (*2*) on sulfuric acid concentration $[H_2SO_4]$ (mol dm^{-3}) in the reaction mixture. Conditions: 45 °C, inlet concentrations of components: $[H_2O_2]$ = 7.19 mol dm^{-3}, [HCOOH] = 19.2 mol dm^{-3}, (*F/V*) = 0.57 h^{-1}. Solid line – calculated values (MODEL 1)

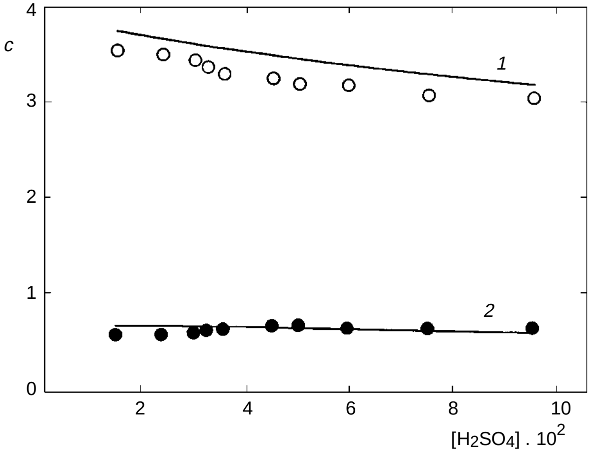

FIG. 5
Dependence of concentration *c* (mol dm^{-3}) of hydrogen peroxide (*1*) and peroxyformic acid (*2*) on sulfuric acid concentration $[H_2SO_4]$ (mol dm^{-3}) in the reaction mixture. Conditions: 45 °C, inlet concentrations of components: $[H_2O_2]$ = 4.9 mol dm^{-3}, [HCOOH] = 13.1 mol dm^{-3}, (*F/V*) = 0.66 h^{-1}. Solid line – calculated values (MODEL 1)

ing from the dissociation of formic and peroxyformic acids. The individual models differ in the reaction orders with respect to formic and peroxyformic acids and in the extent of catalytic effect of H^+ ions on the formation and decomposition of peroxyformic acid and hydrogen peroxide. The best agreement between the measured and calculated data was achieved by adopting the following chemical and kinetic equations.

$$H_2O_2 \quad + \quad HCOOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HCOOOH \quad + \quad H_2O \tag{B}$$

$$HCOOOH \xrightarrow[k_3]{H^+} CO_2 \quad + \quad H_2O \tag{C}$$

$$H_2O_2 \xrightarrow[k_4]{H^+} H_2O \quad + \quad O_2 \tag{D}$$

The rate equations:

$$r_1 = (k_1\, c(H_2O_2)\, c(HCOOH) - k_2\, c(H_2O)\, c(HCOOOH))\, c(H^+) \tag{1}$$

$$r_2 = k_3\, c(HCOOOH)\, c(H^+) \tag{2}$$

$$r_3 = k_4\, c(H_2O_2)\, c(H_2O_2)\, c(H^+)\ . \tag{3}$$

The starting data for the calculation of rate constants involved the following:

- the reactor volume
- the dissociation constants of HCO_2H and HCO_3H ($1.68 \cdot 10^{-4}$ for both)
- the reaction mixture flow rate
- the inlet and outlet concentrations of components.

The presumptions involved a constant volume flow rate of reaction mixture and a reactor with perfect stirring. The rate constants k_i, $i = 1, 2, 3, 4$, were determined by minimizing the sum of squares of deviations of measured and calculated concentrations of hydrogen peroxide and peroxyformic acid at the reactor outlet. The procedure according to ref.[10] was applied to find the minimum of objective function and to evaluate the error of assessment of parameters and the correlation of parameters. All the experimental points shown in Figs 1–5 (38 measurements altogether) were treated simultaneously.

The calculated rate constants (MODEL 1) are as follows:

$k_1 = 1.00 \pm 0.49\ \mathrm{dm^6\ mol^{-2}\ h^{-1}}$
$k_2 = 2.68 \pm 1.57\ \mathrm{dm^6\ mol^{-2}\ h^{-1}}$
$k_3 = 0$
$k_4 = 0.29 \pm 0.04\ \mathrm{dm^6\ mol^{-2}\ h^{-1}}$.

The indicated error in determination of the parameters applies to the confidence interval of 95%. From Figs 1–5 it can be seen that the kinetic model suggested leads to a good agreement between the experimental and calculated values.

The relatively large error in the estimation of parameters k_1 and k_2 in MODEL 1 results from large correlation of these parameters (the coefficient of mutual correlation is 0.993). Therefore, we adopted a kinetic model taking the reactions (*B*) and/or (*A*) as equilibrium ones (MODEL 2) and we tried to find the value of the respective equilibrium constant $K(A)$ and rate constant of reaction (*D*) with rate equation (*3*) – the kinetic constant k_4. The following values were found for MODEL 2:

$\mathrm{K}(A) = k_1/k_2 = 0.32 \pm 0.03$
$k_3 = 0$
$k_4 = 0.29 \pm 0.04\ \mathrm{dm^6\ mol^{-2}\ h^{-1}}$.

Like in the case of application of MODEL 1, in this case too the value of rate constant of decomposition of peroxyformic acid turned out to be statistically insignificant, i.e. zero. The coefficient of mutual correlation of the parameters $K(A)$ and k_4 was 0.14, which positively affected also the accuracy increase of determination of parameters of MODEL 2 as compared with those of MODEL 1. MODEL 2 represents an only slight worsening of description of the experiments as compared with MODEL 1: the sum of residues increased from 2.59 to 3.21.

In conclusion it can be stated that in the through-flow reaction system with the retention times between 1 and 4 h at 45 °C and with the concentrations of hydrogen peroxide and formic acid equal to 2–5 and 12–18 mol $\mathrm{dm^{-3}}$, respectively, an equilibrium concentration of peroxyformic acid is reached (in all the cases below 2.5 mol $\mathrm{dm^{-3}}$), the decomposition of this acid being practically negligible at the given conditions. The decomposition of hydrogen peroxide is catalyzed by acids and is relatively intense, which distinctly lowers the selectivity of formation of peroxyformic acid with regard to hydrogen peroxide (50% in average). The kinetic model described was applied successfully to oxidation of olefins at conditions analogous to those used for the formation of peroxyformic acid.

SYMBOLS

c_i	concentration of the *i*-th component, mol dm^{-3}
k_j	rate constant, dm^6 mol^{-2} h^{-1}
$K(A)$	equilibrium constant of formation of peroxyformic acid
r_i	rate of the *i*-th reaction, mol dm^{-3} h^{-1}

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