Prediction of the Chemical Equilibrium Constant for Peracetic Acid Formation by Hydrogen Peroxide

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ABSTRACT: An expression for temperature dependence of the chemical equilibrium constant for peracetic acid synthesis from acetic acid and hydrogen peroxide in an aqueous solution, derived on the basis of the van't Hoff and Kirchhoff equations, was proposed. The reverse trend of the chemical equilibrium constant vs. temperature was apparent when the predicted values of the constant were compared with experimental ones taken from the literature. However, using the proposed model to calculate the chemical equilibrium constant resulted in better prediction of the equilibrium composition for peracetic acid synthesis at 297.5 K than using experimental data from the literature.

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KEY WORDS: Chemical equilibrium constant for the liquid phase reaction, *in situ* epoxidation, mathematical model, peracetic acid formation.

The production of low-cost plasticizers for poly(vinyl chloride) from natural and renewable sources, such as vegetable oils, is achieved by epoxidation of the main constituent of these oils, unsaturated TG, by percarboxylic acid. Because it is inexpensive, peracetic acid is widely used as the epoxidation reagent and is prepared mostly by the *in situ* method, which is the safest. The *in situ* process involves a heterogeneous system: The acid-catalyzed formation of peracetic acid from acetic acid and hydrogen peroxide occurs in the water phase (using diluted hydrogen peroxide), whereas the epoxidation reaction takes place in the oil phase, as follows (1):

$$CH_3-COOH+H_2O_2 \overset{H^+}{\longleftrightarrow} CH_3-COOOH+H_2O \qquad [1]$$

$$R_1-CH=CH-R_2+CH_3-COOOH \rightarrow R_1-CHOCH-R_2+CH_3-COOH \qquad [2]$$

Depending on the catalyst applied for peracid formation, the system is either two-phase (oil–water) or three-phase (oil–water–ion exchange resin). Additionally, the acid-catalyzed cleavage of oxirane occurs as a side reaction.

Rigorous kinetic models of the three-step reaction system for the epoxidation of unsaturated TG with peracid have been published in the last few years (1–4), although a heterogeneous model of the three-phase system has not. The parameters of the mathematical models that describe the kinetics of the *in situ* epoxidation reaction system can be classified into two groups. The first group contains parameters whose values can only be determined experimentally, such as rate constants. The second comprises parameters that can be determined experimentally, calculated, or estimated, such as chemical equilibrium constants, partition coefficients between phases, mass-transfer coefficients, and interfacial areas. For application of the mathematical model, it is more convenient to use calculated model parameters than to determine them experimentally. For this reason, in the present work we derived the equation for the temperature dependence of the chemical equilibrium constant for the formation of peracetic acid in solution. The validity of the proposed model was tested by comparing the values of the calculated and experimentally determined equilibrium compositions for peracetic acid synthesis.

THEORY

A few two-phase models have been proposed in the literature to describe the catalyzed reaction of peracetic acid formation from acetic acid and hydrogen peroxide under different *in situ* epoxidation conditions.

Rangarajan *et al.* (1) developed a two-phase model with local concentrations (C) of components in particular phases for the *in situ* epoxidation of soybean oil in the presence of sulfuric acid as the catalyst. The chemical equilibrium constant (K_C) for the formation of peracetic acid (P) from acetic acid (A) was given for the water phase (W) by the following equation:

$$K_C^W = \frac{k_+^W}{k_-^W} = \frac{C_P^W C_{H_2O}^W}{C_A^W C_{H_2O_2}^W} \qquad [3]$$

The constant has been calculated using experimentally determined values for the forward ($k_+{}^W$) and reverse ($k_-{}^W$) reaction rate constants. The values obtained for the equilibrium constant ranged between 0.7 and 5 and depended on the H_2O_2 concentration, reactant ratio, and mineral (sulfuric) acid concentration.

In the first, more rigorous kinetic model for the *in situ* epoxidation of soybean oil with peracetic acid in the presence of an ion-exchange resin catalyst (4), the Langmuir–Hinshelwood–Hougen–Watson approach was applied to model the reaction of peracetic acid formation. The use of the overall concentration instead of the local phase concentrations of the reactants and the products, as well as the simultaneous calculation

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*To whom the correspondence should be addressed at Faculty of Technology, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia and Montenegro. E-mail: ssfiser@uns.ns.ac.yu of the kinetic parameters (by fitting the experimental data) instead of determining them successively from the data of separate experiments, led to a very large value for the chemical equilibrium constant for peracetic acid formation (the order of magnitude of 10^9). In contrast to that suggested by the value of K_C^W and a shifting of the equilibrium of peracetic acid formation to the right by the rapid consumption of peracetic acid in the epoxidation reaction, the reaction leading to peracetic acid formation cannot be considered irreversible.

Musante *et al.* (3) provided an extensive model for peracetic acid formation in the presence of an ion-exchange resin. The authors considered selective sorption and resin swelling and concluded that the component concentrations, i.e., activities (a), of all components were different in the water (W) phase from those in the polymer, i.e., resin (R), phases. Accordingly, they defined a two-phase system that consisted of a water phase with N components in equilibrium with a high-viscosity liquid polymer phase, which contained $N + 1$ components. (The $N + 1$st component was the swollen polymer.) They used the UNIFAC (Universal Quasichemical Functional Group Activity Coefficients) liquid–liquid equilibrium (LLE) method of group contributions (5) to determine the activity coefficients of components in the water phase. The extended Flory–Huggins model (6) was applied for the activities of the ith species in the polymer phase:

$$\ln a_i^R = 1 + \ln \omega_i - \sum_{j=1}^{N+1} m_{ij}\omega_j + \sum_{j=1}^{N+1} \chi_{ij}\omega_j - \sum_{j=1}^{N+1}\sum_{k=1}^{j-1} m_{ik}\omega_j\omega_k\chi_{kj} + \eta V_i\left(\frac{5}{3}\omega_R^{1/3} - \frac{7}{6}\omega_R\right) \qquad [4]$$

where N indicates the number of species; a_i^R indicates the activity of the ith species in the resin; ω_i ω_j, ω_k, and ω_R are the volume fractions of the ith, jth, and kth species and of the resin in the polymer phase, respectively; m_{ij} and m_{ik} are the ratios of the molar volume of the ith and jth, and ith and kth species, respectively; V_i is the molar volume of ith species; χ_{ij} and χ_{kj} represent the molecular interaction between components i and j, and k and j, respectively; and η represents the number of moles of active chains per unit volume.

Since the standard Gibbs' free energy of peracetic acid formation cannot be defined with sufficient accuracy (3), the chemical equilibrium constant and the interaction parameters of the Flory–Huggins model (χ_{ij}) were determined simultaneously by processing the experimental data. For these calculations, the thermodynamic equilibrium condition for multicompound sorption given by Equation 5, as well as the component mass balance expressed by Equation 6 and the chemical equilibrium condition defined by Equation 7, was used:

$$a_i^W = a_i^R \qquad i = 1, 2, \ldots, N \qquad [5]$$

$$n_i^R + n_i^W = n_{i,0} + \lambda_i\xi \qquad i = 1, 2, \ldots, N \qquad [6]$$

$$K = (a_P^R a_{H_2O}^R / a_A^R a_{H_2O_2}^R)_{eq} \qquad [7]$$

where n indicates the number of moles, λ is the stoichiometric coefficient of the component, and ξ is the reaction coordinate.

The only question related to the previous model was whether the UNIFAC method could be applied to determine the activity coefficients of components in the mixtures that contained hydrogen peroxide and peracetic acid, as the data for the group contributions of these compounds could not be found in the literature (5). In the absence of specific parameters, in this work H_2O_2 was treated as if it consisted of two OH groups, and CH_3COOOH was treated as if it consisted of CH_3COO and OH groups. The interaction parameters for the OH group were determined from the data on alcohols (5).

As mentioned, it is more convenient to calculate the chemical equilibrium constant as the mathematical parameter in the kinetic model than to determine its values at particular temperatures experimentally. Therefore, this paper proposes a model to predict the chemical equilibrium constant (K) for peracetic acid formation from acetic acid and hydrogen peroxide in the liquid phase.

The chemical equilibrium constant (K) for the reaction in the liquid phase was calculated *via* an integrated form of the van't Hoff equation, using the standard enthalpy change for the reaction in the liquid phase. The latter was determined by integrating Kirchhoff's law using Rowlinson's equation for the heat capacity of the component (reactant or product) in the liquid phase, tabulated polynomial equations for heat capacity in the ideal gas phase (7), and K at a standard temperature, $T_0(K_{T_0})$, determined from the following relation:

$$\Delta G_{T_0}^{0,L} = -R_g T_0 \ln K_{T_0} \qquad [8]$$

where R_g is the ideal gas constant. The standard Gibbs' free energy change for the liquid phase reaction at the temperature T_0 ($\Delta G_{T_0}^{0,L}$) was determined from the standard Gibbs' free energy of formation in the liquid state of all of the reaction components. Because Gibbs' free energy of formation is usually given for the ideal gas state, the equation for values in the liquid state was derived using changes during transformation from the ideal gas state to the liquid state. In this paper, the Soave equation of state (8) was applied. To calculate the molar volume, Rackett's equation (9) was used for the saturated liquid, and Tait's equation (10) was used for the compressed liquid. The properties of the components were taken from Reid *et al.* (7), except for hydrogen peroxide and peracetic acid data, which were from the National Institute of Standards and Technology (11).

The final expression that offers a prediction model for the temperature dependence (in degrees Kelvin) of the chemical equilibrium constant for peracetic acid formation is as follows:

$$K = \exp(12.2324 \ln T - 0.0229913T + 9.70452 \times 10^{-6}T^2 + 3045.76/T - 72.8758) \qquad [9]$$

RESULTS AND DISCUSSION

According to Equation 9, the chemical equilibrium constants for peracetic acid formation calculated at 323, 333, and 343 K were 2.258, 2.091, and 1.952, respectively. Musante *et al.* (3)

TABLE 1
Comparison of Experimentally Determined and Calculated Values of Peracetic Acid Equilibrium Content at 295.7 K

	Experimental	Calculated	
	Ref. 1	Ref. 3	This work
Chemical equilibrium constant at 295.7 K		1.04[a]	2.91[b]
Peracetic acid content (30% H_2O_2), mass%	8.6	5.43	9.49
Peracetic acid content (90% H_2O_2), mass%	46.0	36.56	44.3
RMSD[c]	—	7.04	1.34
AAD[d]	—	6.30	1.28

[a] The correlation used to fit the Musante *at al.* (3) data is as follows: $\ln K = 7.02289 - 2065.575/T$.

[b] Value calculated from Equation 9.

[c] Root mean square deviation, RMSD = $\sqrt{\sum_{i=1}^{N} (y_i^{\exp} - y_i^{calc})^2 / N}$

[d] Average absolute deviation, AAD = $\frac{1}{N}\sum_{i=1}^{N} | y_i^{\exp} - y_i^{calc} |$

reported the values for K, determined experimentally at the same temperatures, of 1.911, 2.18, and 2.778. It is apparent that the K values vs. the temperature trends of the predicted and measured ones are inconsistent, i.e., in the opposite direction.

The validity of the model in Equation 9 for predicting the chemical equilibrium constant was tested by calculating the equilibrium composition at 295.7 K and by comparing it with the equilibrium data reported in the literature for peracetic acid formation by 30 and 90% hydrogen peroxide in the presence of sulfuric acid as the catalyst (12). At the same temperature, the equilibrium composition using data for K values given by Musante *et al.* (3) was also calculated. For that purpose, we extrapolated from the data of Musante *et al.*

Calculation of the equilibrium composition, i.e., determination of the number of moles that were reacted in Equation 1, was performed by solving the nonlinear equations as follows:

$$K = \left(\prod_{i=1}^{N} a_i^{\lambda_i} \right)_{\text{eq}} = \left(\prod_{i=1}^{N} \gamma_i^{\lambda_i} x_i^{\lambda_i} \right)_{\text{eq}} \qquad i = 1, 2, \ldots, N \qquad [10]$$

where γ_i is the activity coefficient and x_i is the molar fraction of the ith species. The modified Newtonian method worked well for this procedure. To calculate the activity coefficient, the UNIFAC LLE model (5) was applied. The presence of sulfuric acid was neglected. The results, in terms of the equilibrium content of peracetic acid, are given in Table 1. The lower SD, compared with those achieved when the data of Musante *et al.* (3) were used, showed that using the derived model to predict the chemical equilibrium constant, given by Equation 9, together with the UNIFAC LLE-calculated activity coefficients in the water phase, predicted the values of equilibrium composition for peracetic acid synthesis reasonably well, even when all previously mentioned simplifications were applied.

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