The nitric acid oxidation of 2-octanol. A model reaction for multiple heterogeneous liquid–liquid reactions

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Abstract

The oxidation of 2-octanol with nitric acid has been selected as a model reaction for a heterogeneous liquid–liquid reaction with an undesired side reaction. 2-Octanol is first oxidized to 2-octanone, which can be further oxidized to carboxylic acids. An extensive experimental program has been followed using heat flow calorimetry supported by chemical analysis. A series of oxidation experiments has been carried out to study the influence of different initial and operating conditions such as temperature, stirring speed and feed rate. In parallel a semi-empirical model has been developed to describe the conversion rates. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

A number of incidents concerning runaway reactions involve systems in which two immiscible phases coexist, generally an organic and an aqueous one. Examples of such systems, in which simultaneously mass transfer and chemical reaction are important, are nitration, sulphonations, hydrolyses, esterifications and oxidations. Experimental studies of the thermal behavior of runaway reactions in a (semi) batch reactor are scarce. Only homogeneous reaction systems are described in literature: the homogeneous, sulfuric acid catalyzed hydrolysis of acetic anhydride, see e.g. [1,2] and the homogeneous, acid catalyzed esterification of 2-butanol and propionic anhydride, see [3]. No experimental systems have been described in detail for a heterogeneous liquid–liquid reaction, in which strongly exothermic side reactions can be triggered. However, in many nitrations it is known that dangerous side reactions can play a role like undesired oxidation reactions, see Camera et al. [4]. They studied the oxidation of ethanol with nitric acid, where decomposition reactions can give rise to explosions.

To study the thermal behavior of a liquid–liquid reaction one has chosen the oxidation of a long chain alcohol with nitric acid. The ketones formed in the oxidation of secondary alcohols are more stable than aldehydes, so one has chosen the oxidation of 2-octanol with nitric acid as a model reaction. Secondary alcohols are also oxidized in the commercial production of adipic acid, in which cyclohexanol is oxidized. This reaction has been studied by Van Asselt and Van Krevelen [5–8] and has been reviewed by Castellan [9].

This work presents experimental data for the oxidation of 2-octanol to 2-octanone and further oxidation products. The main objective is to develop a model to describe the conversion rates of 2-octanol and 2-octanone.

2. Oxidation reactions with nitric acid

Nitric acid is a commonly used oxidizer. Especially alcohols, ketones, and aldehydes are oxidized to pro-
duce the corresponding carboxylic acids, for instance adipic acid, see [10]. The oxidation of cyclohexanol with nitric acid is very similar to the oxidation of 2-octanol, see [9]. The mechanism of these nitric acid oxidations is still not elucidated. Oxidations with nitric acid are in general very complex and usually several intermediates are formed, see e.g. [11]. The elucidation of the real pathways was beyond the scope of the project: therefore, it has been chosen to simplify the description of the conversion rates of 2-octanol and 2-octanone.

The oxidation of 2-octanol occurs in a two-phase reaction system in which a liquid organic phase, containing 2-octanol, is contacted with an aqueous, nitric acid phase. The main organic components during the reactions can be represented as follows:

\[ \text{2-octanol} \rightarrow \text{2-octanone} \rightarrow \text{carboxylic acids} \]

These reactions are further described in more detail in the following paragraphs. Experimental results of nitric acid oxidations from literature will also be used.

### 2.1. Oxidation of 2-octanol

Different reacting species have been proposed like \( \text{N}_2\text{O}_4 \) by Horvath et al. [12], \( \text{NO}^+ \) by Strojny et al. [13] and \( \text{NO}_2 \) by Camera et al. [4]. Castellan [9] concluded that at ambient temperatures the oxidation proceeds mainly via an ionic-molecular mechanism. This indicates that the (\( \text{NO}^+ \)) nitrosonium ion mechanism is applicable for the conditions used in this work. This ion can be formed from nitrous acid and nitric acid through reaction (1):

\[ \text{HNO}_2 + \text{HNO}_3 \leftrightarrow \text{NO}^+ + \text{NO}_3^- + \text{H}_2\text{O} \]  

The oxidations with pure nitric acid exhibit in general a long induction period, see e.g. [5] and [14]. This induction time can be shortened or even eliminated by adding an initiator like \( \text{NaNO}_2 \), which forms nitrous acid:

\[ \text{NaNO}_2 + \text{H}_2\text{O}^+ \rightarrow \text{HNO}_2 + \text{Na}^+ + \text{H}_2\text{O} \]  

The reaction is completely suppressed by addition of urea, which reacts with nitric acid, see e.g. [15], according to:

\[ 2\text{HNO}_2 + \text{CO(NH}_2\text{)}_2 \rightarrow 2\text{N}_2 + \text{CO}_2 + 3\text{H}_2\text{O} \]  

This is in agreement with the above-mentioned formation of a nitrosonium ion or its equivalent.

The oxidation of 2-octanol to 2-octanone proceeds via the formation of an intermediate, which has been identified, as 2-octyl nitrite, using GC-MS. The reaction pathway of the first steps of the oxidation of 2-octanol can be schematically represented as in Fig. 1. After addition of the initiator, \( \text{HNO}_2 \) is formed, the oxidation starts and proceeds autocatalytically. One molecule of \( \text{HNO}_2 \) — or \( \text{NO}^+ \) according to Eq. (1) — is consumed in the first step, while two are formed in the second step. This net formation of an equimolar amount of \( \text{HNO}_3 \) also has been found for the oxidation of cyclohexanol to cyclohexanone, see [5,8].

### 2.2. Oxidation of 2-octanone

2-Octanone can be further oxidized to carboxylic acids. During this reaction an equimolar amount of nitrous acid is consumed, the same as in the oxidation of cyclohexanone, see [5]. The nitric acid oxidation of 2-octanone is studied simultaneously with the oxidation of 2-octanol. Van Asselt and Van Krevelen [5] found different products when oxidizing cyclohexanone with nitric acid and nitrite, compared to the oxidation of cyclohexanol. This probably has been caused by side reactions with the \( \text{NO}_2 \) formed, when a large amount of nitrite is added. The oxidation of 2-octanone is accompanied by the formation of small amounts of unidentified and unstable compounds. These compounds were too unstable to be isolated and identified. The simplified reaction pathways can be represented as in Fig. 2.

Depending on the carbon bond broken, hexanoic acid and acetic acid or heptanoic acid and formic acid are formed. The amount of hexanoic acid as found experimentally is approximately two times the amount of heptanoic acid. The formic acid may further react to \( \text{CO}_2 \), see [16]. During the reaction nitrous acid and nitric acid are consumed.

In the description of the oxidation reactions it is assumed that the reaction proceeds only via the nitrosonium ion \( \text{NO}^+ \). However, at high temperatures above 60°C, the oxidation is known to proceed via a radical mechanism, see [9]. This is outside the operating conditions that will be applied.
3. Derivation of overall conversion rates

The determination of unambiguous stoichiometry and kinetic parameters for oxidation reactions is impossible due to the lacking knowledge of the exact composition of the inorganic compounds in the aqueous reaction phase and the unidentified and unstable intermediates in the organic phase. Hugo and Mauser [17] confirmed this for the nitric acid oxidation of acetaldehyde. One, therefore, has chosen to derive semi-empirical equations for the conversion rates and heat production rates.

The oxidation of 2-octanol (A) to 2-octanone (P) and further oxidation products (X) is simplified to the following two reactions:

$$A + B \rightarrow P + 2B \quad r_{\text{mol}} \quad (4)$$

$$P + B \rightarrow X \quad r_{\text{none}} \quad (5)$$

where B represents the nitrosonium ion which accounts for the autocatalytic behavior. The reactions with the nitrosonium ion take place in the aqueous nitric acid phase, so also the mass transfer rates of the organic compounds have to be taken into account.

This process is schematically represented in Fig. 3. The liquid–liquid system consists of an aqueous acid phase (Aq) with nitric acid and the reacting nitrosonium ion (B), and an organic phase (Org) containing mainly 2-octanol (A), 2-octanone (P) and further oxidation products (X).

The 2-octanol (A) diffuses through the organic phase via the interface into the aqueous acid phase. In the boundary layer and/or bulk of the aqueous phase it reacts with the nitrosonium ion (B) to form 2-octanone (P). The 2-octanone may react with the nitrosonium ion (B) to form carboxylic acids (X) or it is extracted to the organic phase.

In case the transport of the organic compound in the reaction phase is not chemically enhanced and the concentration drop over the film in the reaction phase being relatively small, it is possible to derive an overall reaction rate expression, see [18]:

$$r_i = (1 - \varepsilon)k_{\text{eff}}C_{i,\text{aq}}C_{\text{B,aq}} \quad (6)$$

where \((1 - \varepsilon)\) refers to the volume fraction of the aqueous reaction phase; \(k_{\text{eff}}\) is the effective reaction rate constant. Eq. (6) can be used under the following conditions:

- The rate of chemical reaction is slow with respect to the rate of mass transfer, the rate of mass transfer is not enhanced by reaction, and the reaction mainly proceeds in the bulk of the reaction phase. One must check that the consumption by reaction in the thin boundary layer is negligible, which is justified if \(H_a < 0.3\) holds, see [19]. The Hatta number Ha is defined as:

$$H_a = \frac{\sqrt{k_{\text{eff}}D_iC_{\text{B,aq}}}}{k_{L,\text{aq}}} \quad (7)$$

and \(D_i\) is the diffusivity of the organic compound A and \(k_{L,\text{aq}}\) the mass transfer coefficient for A, both in the aqueous phase.

- The solubility of the organic compound in the aqueous phase is so low, that mass transfer limitations in the organic phase can be neglected. At the interface holds \(C_{i,\text{aq}}^* = mC_{i,\text{org}}^*\).

- The concentration drop over the film of the organic component transferred is less than 5%, see [18], so \(C_{i,\text{aq}}^* \approx C_{i,\text{aq}}\) can be assumed.

If these conditions are fulfilled the conversion rate is independent of the hydrodynamic conditions and interfacial area, hence independent of the stirring rate. The conversion rates are determined by the kinetics of the homogeneous chemical reactions, which can be described by the effective reaction rate constants \(k_{\text{eff,\text{mol}}}\) and \(k_{\text{eff,\text{none}}}\) for the oxidations of 2-octanol and 2-octanone, respectively.

3.1. Kinetic expressions

The effective reaction rate expressions should also account for the effect of temperature and the acid concentration. Oxidation reactions with nitric acid solutions are usually very sensitive towards the acid strength, see [11]. The influence of the acid strength can be accounted for with the Hammett’s acidity function, \(H_\alpha\), see e.g. [20]. So the kinetic constant becomes:
\[ k_{\text{eff}}(T, H_0) = k_{\text{eff},\text{A}} \exp \left\{ - \frac{E_{\text{A}}}{RT} - (m_{H,\text{A}}H_0) \right\} \]  

(8)

For this expression the preexponential factor, \( k_{\text{eff},\text{A}} \), the energy of activation, \( E_{\text{A}} \), \( R \), and Hammett’s coefficient, \( m_{H,\text{A}} \), have to be determined experimentally.

3.2. Conversion rates in a semi-batch reactor

In a semi-batch operation, where 2-octanol is fed to a reactor initially loaded with nitric acid, the overall balances list:

— for the 2-octanol, \( A \):

\[ \frac{d\eta_A}{dt} = \varphi_{\text{dos}} C_{A,\text{dos}} - r_{\text{mol}} V_t \]  

(9)

where \( \varphi_{\text{dos}} \) is the volumetric flow rate of the feed dosed into the reactor.

— for the 2-octanone, \( P \):

\[ \frac{d\eta_P}{dt} = r_{\text{mol}} V_t - r_{\text{none}} V_t \]  

(10)

— for the carboxylic acids, \( X \):

\[ \frac{d\eta_X}{dt} = r_{\text{none}} V_t \]  

(11)

— for the nitric acid, \( N \):

\[ \frac{d\eta_N}{dt} = -r_{\text{mol}} V_t - r_{\text{none}} V_t \]  

(12)

The conversions are defined, on the basis of the total amount of 2-octanol fed, \( n_{A1} \):

\[ \bar{\xi}_P = \frac{n_P}{n_{A1}} \quad \bar{\xi}_X = \frac{n_X}{n_{A1}} \]

The mass balances above can be made dimensionless, analogous to Steenma and Westerterp [18], as follows:

\[ \frac{d\bar{\xi}_P}{d\theta} = m_A k_{\text{eff},\text{A}} \varphi_{\text{dos}} C_{A,\text{dos}} (\theta - \bar{\xi}_P - \bar{\xi}_X) \frac{\bar{\xi}_P}{\theta} \]  

(14)

\[ \frac{d\bar{\xi}_X}{d\theta} = m_P k_{\text{eff},\text{none}} \varphi_{\text{dos}} C_{A,\text{dos}} (\bar{\xi}_P) \frac{\bar{\xi}_P}{\theta} \]  

(15)

in which \( \theta \) is the dimensionless dosing time \( t/t_{\text{dos}} \). After the end of the dosing \( \theta = 1 \) in Eqs. (14) and (15) and the reaction proceeds as in a batch reactor. The boundary conditions for these differential equations and the corresponding heat balance will be discussed later.

It is assumed the volumes of the aqueous phase and the organic phase are not affected by reaction. During the oxidation of 2-octanol and 2-octanone the average molecular weight of the organic compounds does not change much, so this assumption is justified. The assumption of low solubility of reactants and products in the aqueous phase, which also may result in a change in volume, has to be validated.

In this simplified representation of the oxidation reactions, Eqs. (4) and (5), the reactions can be described with only two dimensionless partial mass balances. The model of Eqs. (9)–(15) will be used to obtain the relevant kinetic parameters and to simulate the experimental conversion rates.

4. Experimental set-up

4.1. Reaction calorimeter

The oxidation reactions have been studied in a reaction calorimeter RC1 of Mettler Toledo, which contains a jacketed reactor vessel. Using the reaction calorimeter the flow of the heat \( Q_{\text{cool}} \) is determined, which is transferred through the wall of the vessel and which is proportional to the temperature difference between the reactor contents \( T_r \) and the coolant temperature \( T_{\text{cool}} \):

\[ Q_{\text{cool}} = UA \cdot (T_{\text{cool}} - T_r) \]  

(16)

The proportionality factor \( UA \) has to be determined by calibration, which is done by introducing via an electrical heating element a known amount of energy \( Q_c \):

\[ UA = \frac{Q_c}{(T_r - T_{\text{cool}})} \]  

(17)

The reaction calorimeter enables an accurate measurement of the temperatures of the reactor contents and of the coolant.

The heat balance for the reactor operating in the semi-batch mode can be written as:

\[ \frac{dT}{dt} + \frac{dT_w}{dt} \Gamma_w = Q_R + Q_{\text{dos}} + Q_{\text{cool}} + Q_{\text{stir}} + Q_{\text{inf}} \]  

(18)

where \( \Gamma_r \) is the thermal capacity of the reaction mixture and internal devices in the reactor, and \( \Gamma_w \) is the thermal capacity of the reactor wall. The wall temperature is estimated by: \( T_w = 1/2(T_r + T_{\text{cool}}) \). The different heat flows taken into account are \( Q_R \) by the chemical reaction, \( Q_{\text{dos}} \) by mass addition, \( Q_{\text{cool}} \) to the coolant, \( Q_{\text{stir}} \) by the agitation and \( Q_{\text{inf}} \) to the surroundings.

4.2. Experimental set-up and experimental procedure

The experimental set-up is shown in Fig. 4. The RC1 (1) contains a jacketed 1-l glass vessel of the type SV01. The main dimensions of the reactor are given in Fig. 5. The reactor content is stirred by a propeller stirrer with a diameter of 0.04 m. The stirring speed is adjusted to 700 rpm. For further details and drawings of the RC1 see [21,22].

The reactor is operated in the semi-batch mode under isothermal conditions. To operate below room tempera-
ture an external cryostatic bath (2) of the type Haake KT40 has been installed. Before the experiment is started, the equipment is flushed with N\textsubscript{2}. The reactor is initially filled with 0.4 kg of HNO\textsubscript{3}-solution. First the effective heat transfer coefficient is determined with the electrical heater with a thermal power of 5 W. After that a small amount of 0.1 g NaNO\textsubscript{2} is added as initiator. As soon as the temperature of the reactor has reached a constant value, the feeding of reactant 2-octanol is started by activating the dosing system. The dosing system contains the supply vessel, which is located on a balance of the type Mettler pm3000 (3), a Verder gear pump (4) and a Mettler dosing controller RD10 (6). The feed rate is kept constant in the range of 0.05–0.4 kg/h. The nitric acid and organic solutions are immiscible and form a dispersion. The nitric acid remains the continuous phase during the whole experiment. During the oxidation of 2-octanol NO\textsubscript{X}-gases are formed, which accumulate above the reaction mixture and are let off through an opening in the reactor lid to the scrubber (5) to be washed with water. After addition of 0.1 kg 2-octanol the dosing is automatically stopped and the experiment is continued for at least two times the total dosing time. The experiment is then brought to an end by heating up the reactor contents to complete the conversion and after that again a determination of the effective heat transfer coefficient.

Also the temperatures of the feed and of the surroundings are measured and together with the feed flow rate monitored and stored by a computer. When the reactor temperature exceeds a certain value the computer automatically triggers an emergency cooling program and opens the electric valve in the reactor bottom to dump the reactor content and quench it in ice (8). During an experiment 4 to 10 samples of the dispersion are taken via a syringe, as indicated by (7) in Fig. 4.

4.3. Chemical treatment and chemical analysis

During an experiment samples of the dispersion are taken of approximately 1 ml, using a syringe. The dispersion, once in the syringe, separates directly in two phases.

The total amount of strong and weak acids in the aqueous phase is determined by titration with a 0.1 M NaOH-solution in an automatic titration apparatus of the type Titrino 702 SM of Metrohm.

During the reaction some unstable and unidentified compounds are formed and the composition of an untreated sample changes with time. Therefore, the samples of the organic phase are contacted with demineralized water to stabilize the sample and remove the nitric acid from the organic phase. The organic phase is then analyzed by gas chromatography using a Varian 3400 with a FID detector. The injector and detector temperatures are set at 240°C. The column is packed with Carbopack C and is operated at 190°C with N\textsubscript{2} as carrier gas. The concentrations of 2-octanol, 2-octanone, hexanoic acid and heptanoic acid are determined using reference samples and an integrator of type HP3392A.

To study the influence of temperature the oxidation reaction has been investigated in the temperature range of 0–40°C, for dosing times of 900–7200 s, for 100 g of 2-octanol and an initial nitric acid concentration of 60 wt.%. Furthermore a series of experiments has been carried out in the range of 50–65 wt.% with a dosing time of 1800 s to study the influence of the initial nitric acid concentration. A total of 33 runs were carried out to obtain kinetic data.

An example of an experimental run is shown in Fig. 6. Two peaks can be observed in the temperature of the reactor as a function of time. The first peak is small and is caused by the addition of the initiator. The second one is caused by the start of the reaction; its deviation from the temperature set remains usually below 2°C for a dosing times of 30 min and longer. Deviations from isothermcity were larger for experiments with a short dosing time of 15 min. In this case, at temperatures
above 25°C the heat production rate was so large that isothermal operation became impossible. In Fig. 6b the calculated heat production rate is plotted as function of time. The maximum in the heat production rate is an easily to be detected, sensitive measure of the course of the reaction. It will be used in some comparisons further on.

For the same experiment the molar amounts of the organic compounds in the organic phase and the total molar amounts of weak and strong acids in the aqueous nitric acid solution are given as a function of time in Fig. 7. 2-Octanol accumulates in the reactor and a part of the dosed 2-octanol reacts to 2-octanone, which is partly converted into carboxylic acids. As a result, the yield of 2-octanone exhibits a maximum.

The distribution of 2-octanol and 2-octanone has been estimated on the basis of TOC analysis of a saturated 60 wt.% nitric acid solution and $m_A = 0.005$ and $m_P = 0.006$ for 2-octanol and 2-octanone, respectively. The distribution coefficients of the carboxylic acids are estimated on the basis of gas chromatography analysis and $m \approx 0.01$ for both heptanoic acid and hexanoic acid and $m \approx 1.5$ for acetic acid. Thus, in view of the low solubilities for 2-octanol, 2-octanone, heptanoic acid and hexanoic acid, the amounts of organic compounds in the aqueous phase can be neglected. The simultaneously formed acetic and formic acids will be distributed over both the organic phase and aqueous phase and, as a result, the volume of aqueous phase will increase as the reaction proceeds. At the same time a considerable quantity of nitric acid will dissolve into the organic phase. The overall effect on the volume ratio is small, since hardly any change in volume is observed during the experiments.

The aqueous phase contains strong and weak acids. The strong acid is nitric acid, the different weak acids could not be distinguished in the titration method used. The weak acids probably consist of acetic and formic acids as well as an amount of inorganic acids like HNO$_2$.

Due to the extraction of nitric acid a part is not available for reaction. The amount of nitric acid in the organic phase is determined by titration with a 0.1 M NaOH solution and is approximately 2.5 mol/kg organic phase for 50–60 wt.% HNO$_3$. Therefore the amount of strong acid in the aqueous phase, determined by titration as shown in Fig. 7b, appears to decrease faster then one may expect based on the stoichiometry of the reactions.
Fig. 8. Maximum heat production rate vs. stirring speed at 20, 30 and 40°C. Isothermal semi-batch experiments with an initial load of 0.4 kg 60 wt.% HNO₃ and 0.1 g NaNO₂. Addition of 100 g 2-octanol in a dosing time of 30 min.

5. Experimental results

The kinetic parameters of the proposed model can be found by measuring the conversion rates by means of thermokinetic measurements in the calorimeter in combination with chemical analyses. Before the kinetic parameters are evaluated the reaction regime has to be identified.

5.1. Identification of reaction regime

5.1.1. Effect of agitation

If the conversion rate in a liquid–liquid reaction is not influenced at all by mass transfer resistances, it should be independent of the interfacial area and, hence, of the degree of agitation. The influence of the stirring rate on the conversion rate has been experimentally determined at 20, 30 and 40°C.

In Fig. 8 the measured maximum heat production rate is plotted against the stirring speed. The maximum heat production initially increases with stirring speed, but becomes independent of the agitation above 300 rpm. At a stirring speed below 150 rpm the reaction mixture separates into two liquid phases and it becomes well dispersed at stirring rates above 500 rpm, as can be visually observed. Between 150 and 500 rpm a certain volume of undispersed organic phase is visible above the dispersion and the heat production rates fluctuate in time.

For a stirring rate of above 500 rpm evidently the mass transfer resistance $1/k_L a$ does not play a role anymore. One, therefore, has chosen a stirring rate of 700 rpm for all the experiments.

5.1.2. Effect of phase volume ratio

By assuming the nitrosonium ion being the reactive species it is likely that the reaction takes only place in the aqueous acid phase. The conversion rate is usually proportional to the volume of reacting phase, according to: $R = k C_A C_B V_R$, where $C_A$ and $C_B$ are the concentrations of the reacting compounds in the reaction phase with volume $V_R$. On the other hand, the reaction phase can be identified by varying the volume of the phases and keeping all other parameters constant, see e.g. [23,24]. However, for the autocatalytic reaction, complications arise when the concentration of nitrosonium ion $C_B$ has to be kept constant, while the volume of the aqueous phase $V_R$ is changed. The number of moles of nitrosonium ion $n_B = C_B V_R$ is equal to the number of moles of product in the non-reaction phase $n_P = C_p V_d$. The concentration of nitrosonium ion is therefore equal to $C_B = C_p V_d / V_R$ and consequently the conversion rate is also equal to $R = k C_A C_p V_d$. Thus a larger initial volume of aqueous phase $V_R$ will be accompanied by a lower concentration of nitrosonium ion $C_B$ and as a result there is no change in conversion rate.

The oxidation reaction has been carried out with different volumes of the aqueous reaction phase as is shown in Table 1. The experimental results are plotted in Fig. 9 and show an increase in heat production rate with an increasing volume of nitric acid. This increase in the maximum heat production rate can be explained entirely by the effect of the acid strength on the kinetic constant $k$: the nitric acid remains at a higher concentration level for a larger concentration level for a larger initial volume, as its excess is larger. Thus a larger volume of reaction phase $V_R$ has no effect on the part $C_A C_B V_R$ as mentioned above. This confirms nitric acid being the reaction phase.

Table 1

<table>
<thead>
<tr>
<th>Run</th>
<th>Volume of acid phase (ml)</th>
<th>Volume of organic phase (ml)</th>
<th>Feed concentration 2-octanol (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>293</td>
<td>120</td>
<td>6.40</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>120</td>
<td>6.40</td>
</tr>
<tr>
<td>3</td>
<td>525</td>
<td>120</td>
<td>6.40</td>
</tr>
<tr>
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<tr>
<td>6</td>
<td>295</td>
<td>225</td>
<td>3.64</td>
</tr>
<tr>
<td>7</td>
<td>295</td>
<td>278</td>
<td>2.77</td>
</tr>
</tbody>
</table>

* All experiments with initially 60 wt.% HNO₃ and 0.1 g NaNO₂ at 25°C, in the semi-batch mode with a dosing time of 30 min.
The above phenomena also support the assumed ionic mechanism via NO⁺ in the aqueous acid phase. Thus, although some reaction may take place in the organic phase its contribution to the overall rate will be neglected. So one assumed that the reaction only takes place in the aqueous, nitric acid phase.

5.2. Determination of kinetic parameters

Now the kinetic parameters can be determined using the conversion rate expressions for slow liquid–liquid reactions, provided the heats of reaction are known.

5.2.1. Determination of effective heats of reaction

The heat production is determined by the chemical reactions and physical phenomena like dilution, etc. The heat production rate by n chemical reactions can be written as:

$$Q_R = \sum_{i=1}^{n} r_i \Delta H_i V_r$$

(19)

The amount of heat released by the reaction ΔE is determined by integrating the experimentally measured heat generation rate $Q_R$ over the reaction time:

$$\Delta E_{calorimeter} = \int_0^t Q_R \, dt = \int_0^t (Q_{\text{mol}} + Q_{\text{none}}) \, dt$$

(20)

where $Q_{\text{mol}}$ and $Q_{\text{none}}$ are the heat generated by the oxidation of 2-octanol and 2-octanone, respectively. The results of the chemical analyses are used to calculate the amounts of heat generated by both reactions separately:

$$\Delta E_{\text{analyses}} = \Delta H_{\text{eff,nol}} \cdot (\zeta_P + \zeta_X) \cdot n_{A1}$$

$$+ \Delta H_{\text{eff,none}} \cdot \zeta_X \cdot n_{A1}$$

(21)

The effective heats of reaction $\Delta H_{\text{eff,nol}}$ and $\Delta H_{\text{eff,none}}$ are obtained using the complete set of isothermal experiments and by minimizing the deviation between the amount of heat measured by the calorimeter,
\[ Q_r = Q_{\text{mol}} + Q_{\text{none}} = r_{\text{mol}} V_t \cdot \Delta H_{\text{eff,mol}} + r_{\text{none}} V_t \cdot \Delta H_{\text{eff,none}} \]  

On the basis of the chemical analyses the conversion rates can be obtained by differentiation of a polynomial fit of the measured data points, as is shown in Fig. 13 and using the following equations:

\[ (r_{\text{mol}} V_t) = \frac{n_A}{T_{\text{dos}}} \left( \frac{d_x^p}{d\theta} + \frac{d_x^X}{d\theta} \right) \]  

and

\[ (r_{\text{none}} V_t) = \frac{n_A}{T_{\text{dos}}} \frac{d_x^X}{d\theta} \]

The sampling frequency during an experiment was usually once per 15 min, which results in 5–10 samples per run. Due to this limited amount of sampling data points, not always a useful polynomial expression could be obtained for the 2-octanone (P) concentration. The concentration of the further oxidation products (X) increases approximately linearly with time under the experimental conditions applied and good polynomial functions could be found, as shown in Fig. 13. To improve upon the accuracy of the conversion rate of 2-octanol to 2-octanone the calculated heat of formation is in good agreement with the experimentally determined reaction heat. For the oxidation of 2-octanone to carboxylic acids a 16% difference was found; this is probably the result of endothermic decomposition reactions, which produce NOX gases, and which have not been taken into account.

5.2.2. Determination of the model parameters

The kinetic constants for the proposed model can now be found by comparing the experimental conversion rates of 2-octanol and 2-octanone and the proposed model equations. During an experiment the conversion rates can be determined by evaluating the heat flow measurements or the results of the chemical analyses, using Eq. (19) and the determined effective heats of reaction as listed in Table 2. The total heat production rate in the reactor \( Q_R \) is equal to:

\[ Q_R = Q_{\text{mol}} + Q_{\text{none}} = r_{\text{mol}} V_t \cdot \Delta H_{\text{eff,mol}} + r_{\text{none}} V_t \cdot \Delta H_{\text{eff,none}} \]  

The sampling frequency during an experiment was usually once per 15 min, which results in 5–10 samples per run. Due to this limited amount of sampling data points, not always a useful polynomial expression could be obtained for the 2-octanone (P) concentration. The concentration of the further oxidation products (X) increases approximately linearly with time under the experimental conditions applied and good polynomial functions could be found, as shown in Fig. 13. To improve upon the accuracy of the conversion rate of 2-octanol to 2-octanone the total conversion rate from the heat flow measurements \( Q_R \) is combined with the information of chemical composition of the further oxidation products (X) as function of time. The conversion rate of 2-octanol \( r_{\text{mol}} V_t \) can also be expressed as:

\[ (r_{\text{mol}} V_t) = \frac{(Q_R - r_{\text{none}} V_t \cdot \Delta H_{\text{eff,none}})}{\Delta H_{\text{eff,mol}}} \]  

For every run in the reaction calorimeter first the conversion rate of the carboxylic acids \( r_{\text{none}} V_t \) is evaluated using Eq. (24) and the polynomial expression. Then the conversion rate of 2-octanone \( r_{\text{none}} V_t \) is evaluated by Eq. (25). Combining these conversion rates from Eqs. (24) and (25) with the mass balances Eqs. (14) and (15) gives:
All parameters in the Eqs. (26) and (27) are known, except $m_{A_k,\text{eff, tol}}$ and $m_{P_k,\text{eff, none}}$. The kinetic constants of the proposed expression of Eq. (8) are obtained by non-linear regression using the complete set of isothermal experiments and fitting the Eqs. (26) and (27) to the results of Eqs. (24) and (25). The results are listed in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$m_{k_{\text{eff, tol}}}$ (l/mol·s)</th>
<th>$E_{\text{eff}}/R$ (K)</th>
<th>$m_{H_0,\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-octanol</td>
<td>$1 \times 10^3$</td>
<td>11 300</td>
<td>6.6</td>
</tr>
<tr>
<td>→ 2-octanone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-octanone</td>
<td>$1 \times 10^{10}$</td>
<td>12 000</td>
<td>2.2</td>
</tr>
<tr>
<td>→ products</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 14. Effect of acid strength on the reaction rate constants for the oxidation of 2-octanol and 2-octanone, respectively. Lines calculated according to Eq. (8) and parameters from Table 3 for $T = 20^\circ\text{C}$.

The effective kinetic constant depends on temperature and acid strength. To discuss the influence of these parameters on the kinetic constants the value of $m_{k_{\text{eff}}}$ is measured for both reactions. The kinetic constant is very sensitive to the nitric acid concentration: below 40 wt.% the reaction is so slow that hardly any heat production is measurable, while above 65 wt.% the reaction becomes too fast. Expressed as an exponential order in the concentration of HNO$_3$, the exponent would be as high as 12 for the oxidation of 2-octanol. This has no physical or chemical meaning, so Hammett’s acidity function is used, see [20]. Fig. 14 shows a plot of $m_{k_{\text{eff}}}$ at 20°C as a function of Hammett’s acidity function $H_0$. The slope of ln($m_{k_{\text{eff}}}$) versus $H_0$ is 1.25 and 0.41 for the oxidations of 2-octanol and 2-octanone, respectively. These values can be compared to those reported in literature. Ogata et al. [14] found a slope of 0.95 for the nitric acid oxidation of benzyl alcohol, while for the oxidation of benzaldehyde a value of 0.43 has been reported, see [25]. The oxidation of 2-octanol depends more strongly on the nitric acid concentration then the oxidation of 2-octanone. This has also been found for the oxidation of benzyl alcohol and benzaldehyde respectively as described above. Therefore, to increase the yield of 2-octanone the concentration of nitric acid should be high. The term $m_{H_0,\text{eff}}$ accounts for the acidity effect on the conversion rate including the acidity influence on the solubility, which is known to increase with increasing HNO$_3$ concentration, see [26].

In Fig. 15 the value of $m_{k_{\text{eff}}}$ is plotted at 60 wt.% HNO$_3$ as a function of temperature. The term $E_{\text{eff}}/R$ accounts for the temperature influence on the conversion rate, including the temperature influence on the solubility and, more important, the Hammett acidity. The latter is only well tabulated for HNO$_3$-solutions at 25°C, see [20], but some data points at 20°C indicate an increasing acidity with increasing temperature, hence the value of $E_{\text{eff}}/R$ is overestimated.

Although no experimental data on the oxidation of 2-octanol or 2-octanone have been published, comparable data can be found in literature for other nitric acid oxidations. The reported data on energy of activation vary from 9000 K for the oxidation of methoxyethanol, see [13], to 14 230 K for benzyl alcohol, see [14]. The same range is found for aldehydes or ketones: from 8000 K for cyclohexanone, see [7] to 14 400 K for benzaldehyde, see [25].

When the determined values of $m_{k_{\text{eff}}}$ for both reactions are compared, an equal trend is observed with respect to temperature. As the energy of activation has comparable values for the oxidation of alcohols, aldehydes or ketones, selectivity can not be influenced by temperature.
6. Simulation of isothermal runs

The mathematical model for the oxidation rates has been tested using the kinetic parameters as described above. The mass balances Eqs. (14) and (15) are expressed as two differential equations and can be solved simultaneously using a fifth order Runge–Kutta method with an adaptive step size control, see [27]. In view of the autocatalytic behavior, whereby some reaction product must be present before the reaction can start, an initiator has to be added. For all experiments an addition of 0.1 g NaNO₂ has been chosen. This is, as experimentally found, the minimum amount to be added to ensure the reaction starts immediately. To solve the differential equations and to account for the initial reaction rate, an initial concentration of 2-octanone has to be taken, which is an optimizing problem. The initial reaction rates as experimentally determined and calculated are in good agreement provided an initial concentration of 2-octanone equal to 3.5% is taken. Thus, the boundary conditions for these differential equations are: \( \zeta_{P_0} = 0.035 \) and \( \zeta_{X_0} = 0 \) at \( \theta = 0 \). The differential equations together with the kinetic parameters in Table 3 can now be used to simulate the experiments. Fig. 16 shows the experimentally determined and simulated heat production rates as a function of time. The simulated heat production rates \( Q_{\text{nol}} \) and \( Q_{\text{none}} \) are plotted for the separate reactions. Also both, the simulated and experimental, total heat production rates \( Q_R = Q_{\text{nol}} + Q_{\text{none}} \) are plotted. The measured and simulated conversion-time profiles for 2-octanol, 2-octanone and carboxylic acids are shown in Fig. 17 for the same series. The 2-octanol was added in 30 min to 60 wt.% HNO₃ at a temperature of 10, 20 and 40°C, respectively. One can observe that the heat generation rate increases with increasing temperature, which is the result of both the increasing conversion rate of 2-octanol as well as the increasing rate of the more exothermic oxidation of 2-octanone.

![Fig. 16. Experimental total heat production rate \( Q_{R,\text{experimental}} \) (thick line) and simulated (thin lines) heat production rates \( Q_{\text{nol}}, Q_{\text{none}} \) and \( Q_{R,\text{simulated}} = Q_{\text{nol}} + Q_{\text{none}} \). Isothermal semi-batch experiments at a temperature of 10, 20 and 40°C, respectively, with an initial load of 0.4 kg 60 wt.% HNO₃ and 0.1 g NaNO₂. Addition of 0.1 kg 2-octanol in a dosing time of 30 min.](image1)

![Fig. 17. Experimental (dots) and simulated (lines) conversions of 2-octanol (\( \bullet, \cdots \cdot \)), 2-octanone (\( \blacksquare, \cdots \cdot \)) and carboxylic acids (\( \blacktriangle, \cdots \cdot \)). Isothermal semi-batch experiments with experimental conditions as for Fig. 16.](image2)
7. Model validation and limitations

The process of mass transfer with chemical reaction during the oxidations of 2-octanol and 2-octanone with nitric acid has been modeled by assuming that the conversion rate is not affected by mass transfer rates. The verification of the assumptions described in Section 3 regarding this mass transfer rates is discussed below:

7.1. Slow reaction, \( Ha < 0.3 \)

The Hatta numbers are calculated for both reactions and listed in Table 4 as a function of temperature. These values have been obtained for \( C_{NaNO_2,0} = 4.9 \cdot 10^{-3} \text{ M} \), \( C_{HNO_3,0} = 13.0 \text{ M} \) and the stirring rate is 700 rpm. The diffusivity coefficients have been calculated using the relation of Wilke and Chang [28] together with the relation of Cox and Strachan [29] to correct for nitric acid mixtures. The estimation of the mass transfer coefficients will be discussed in the next paragraph.

The calculated Hatta numbers for the oxidation of 2-octanol to 2-octanone (P) indicate that the transfer rates are not enhanced by chemical reaction as long as the temperature is below 20°C. The conversion rate of 2-octanone to further oxidation products is not chemically enhanced in the whole range of applied temperatures.

If the reaction is not slow compared to mass transfer, the enhancement can be estimated by the expression of Danckwerts, see e.g. [19]:

\[
E_A = \sqrt{1 + Ha^2}
\]  

(28)

The deviations are within 5 and 10% up to a temperature of 10 and 20°C, respectively. The deviation is slightly higher at 40°C: 17%, but still reasonably small as also experimentally demonstrated by the influence of stirring speed.

7.2. Mass transfer resistance in the organic phase negligible

The mass transfer resistance in the organic phase is zero if the phase consists of pure reactant without solvent as in the case of the oxidation of 2-octanol. As the reaction proceeds, 2-octanone is formed and dilutes the organic phase. Thus the validity of the neglect of the mass transfer resistance in the organic phase must be examined. This assumption holds, see [19], if:

\[
\frac{k_{L,org}}{k_{L,Aq}} \gg 1
\]

(29)

The mass transfer coefficients \( k_{L,Aq} \) for 2-octanol and 2-octanone in the continuous, aqueous phase can be estimated with the empirical correlation of Calderbank and Moo-Young [30] as discussed in detail by Van
Woezik and Westerterp [31]. A typical value of the mass transfer coefficients for both 2-octanol and 2-octanone in the continuous phase is \( k_{L,Aq} = 20 \times 10^{-6} \) m/s for the range of experimental conditions. This value is in agreement with the value reported by Chapman et al. [32]. They found experimentally \( k_l = 10.3 \times 10^{-6} \) m/s for toluene in a HNO\(_3\)/H\(_2\)SO\(_4\) solution.

In view of the low solubility of the organic compounds in nitric acid with \( m_A = 0.005 \) and \( m_p = 0.006 \) for 2-octanol and 2-octanone, respectively, and the mass transfer coefficient in liquid–liquid dispersions of the same order of magnitude, see e.g. [33] and [34], this gives for \( k_{L,org}/(k_{L,Aq}m) \) a value of approximately 200. Therefore, the mass transfer resistance in the organic phase is negligible for the transport of both 2-octanol and 2-octanone.

7.3. The concentration drop over the film is negligible

The concentration drop from \( C_{i,Aq}^* \) to \( C_{i,Aq} \) is relatively more important if mass transfer resistance in the aqueous phase is higher. When the concentration drop is more than say 5%, the simple approximation \( C_{i,Aq}^* \approx C_{i,Aq} \) starts to lead to inaccuracies, see [18]. To check this approximation it is possible to compare the rate of mass transfer with the chemical reaction, see [35]:

\[
Ja = k_l(C_{i,Aq}^* - C_{i,Aq})a \tag{30}
\]

\[
Ja = (1 - \varepsilon)k_{eff,Aq}C_{i,Aq} \tag{31}
\]

where \( a \) is the interfacial area per unit volume of reactor content. The combination of both equations gives:

\[
(1 - \varepsilon)k_{eff,Aq}C_{i,Aq} = \frac{C_{i,Aq}^*}{k_l a} - 1 \tag{32}
\]

Hence, in the case where \( C_{i,Aq}^* \approx C_{i,Aq} \) it must be checked whether \( (1 - \varepsilon)k_{eff,Aq}/k_l a \ll 1 \). The total interfacial area is estimated by means of the Sauter mean drop diameter, \( d_{s2} \), which is defined as:

\[
\frac{d_{s2}}{D_{stir}} = A(1 + Be)We^{-0.6} \tag{34}
\]

where \( D_{stir} \) is the impeller diameter, \( \varepsilon \) is the volume fraction of dispersed phase, \( A \) and \( B \) are empirical constants, which must be determined experimentally for a given reactor set-up and liquid–liquid system, see [31]. \( We \) is the Weber number, defined as:

\[
We = \frac{N^2D_{stir}^3\rho_c}{\sigma} \tag{35}
\]

where \( N \) is the stirring rate, \( \rho_c \) is the density of the continuous phase and \( \sigma \) is the interfacial tension. Eq. (34) has been used by numerous workers, whereby the values of \( A \) and \( B \) depend on the geometry. With the used values for \( A \) and \( B \) reasonable values for the drop size are obtained. This is sufficiently accurate to estimate the validity of the concentration drop over the film.

The interfacial tension is predicted using the empirical correlation of Good and Elbing [36]:

\[
\sigma_{i2} = \gamma_1 + \gamma_2 - 2\phi_{12}\sqrt{\gamma_1\gamma_2} \tag{36}
\]

where \( \phi_{12} \) is an experimentally determined interaction parameter and \( \gamma_1 \) and \( \gamma_2 \) are the surface tensions of the pure components. The interaction parameter \( \phi_{12} \) is not known for 2-octanol. One has therefore used the value for \( n \)-octanol, see [36], which is equal to \( \phi_{12} = 0.97 \). The surface tensions for both 2-octanol and 2-octanone are equal to 0.026 N/m at 20°C, see [37], and for a 60 wt.% HNO\(_3\) solution it is equal to 0.063 N/m, see [38]. The liquid–liquid interfacial tension between 2-octanol, 2-octanone or a mixture of both with a 60 wt.% nitric acid solution is thus equal to \( \sigma = 0.010 \) N/m. This can be compared to the experimental value between octanol and water of \( \sigma = 0.0085 \) N/m, as measured by Van Heuven and Beek [39].

The Weber-number is now equal to \( We = 1175 \). The interfacial area increases with the hold-up of the organic phase for the system from 8000 to 15 000 m\(^2\)/m\(^3\). Typical values of \( (1 - \varepsilon)k_{eff,Aq}/k_l a \) are listed in Table 5 as a function of temperature.

The assumption of a negligible concentration drop over the film for 2-octanone is valid. For 2-octanol this is not true and the simple approximation \( C_{i,Aq}^* \approx C_{i,Aq} \) leads to inaccuracies. The deviations are within 5 and 10% up to a temperature of 10 and 20°C, respectively.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( (1 - \varepsilon)k_{eff,nol}C_{i,Aq}/k_l a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
</tr>
<tr>
<td>20</td>
<td>0.07</td>
</tr>
<tr>
<td>30</td>
<td>0.15</td>
</tr>
<tr>
<td>40</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* Isothermal oxidation experiments with \( N = 700 \) rpm and initially 60 wt.% HNO\(_3\) and 0.1 g NaNO\(_2\).
Fig. 19. Experimental (—) and simulated (· · ·) reactor temperatures in some isoperibolic semi-batch experiments with varying coolant temperature with $T_0 = T_{\text{cool}}$. Initial load of 60 wt.% HNO$_3$ and 0.1 g NaNO$_2$. Addition of 100 g 2-octanol in a dosing time of 120 min.

The isoperibolic experiments were carried out in the same way as the isothermal runs, except that the calorimeter now is operated with a constant jacket temperature. In Fig. 19 the temperature profiles are plotted for five isoperibolic experiments with different jacket temperatures: the experimental profiles are in good agreement with the simulations. In Fig. 20 the temperature profiles are plotted for four isoperibolic experiments with different jacket temperatures and a faster dosing rate. As can be seen one is working in a parametric sensitivity region, where the maximum reactor temperature, $T_{\text{max}}$, is sensitive towards the cooling temperature $T_{\text{cool}}$.

Under these conditions even a small deviation between model and actual parameters will lead to large discrepancies. At higher temperatures the model overestimates the reactor temperature, which can be attributed to evaporation of the nitric acid solution, which has not been incorporated in the model. However, the simulated and the experimental results show the same thermal behavior. This thermal behavior of the oxidation reaction will be discussed in more detail and under varying experimental conditions in a future communication, see [40].

8. Discussion and conclusions

The main objective of this paper is to determine the kinetic parameters of the model proposed to describe the heterogeneous oxidation of 2-octanol to 2-octanone and the unwanted, further oxidation reactions to carboxylic acids. The oxidation of 2-octanol and 2-octanone with nitric acid exhibits the typical features of nitric acid oxidation reactions, like a long induction time without initiator; autocatalytic reaction; strong dependence of mineral acid concentration and high energy of activation, see [11]. Although the main phenomena of nitric acid oxidation reactions are well known the exact mechanism is still not elucidated. There is a limited knowledge of the exact chemical structure of the compounds in the aqueous reaction phase and of a number of unknown, unstable compounds in the organic phase. As a consequence of this a strong model reduction was necessary to describe the overall reaction rates. This model reduction in this case gave satisfactory results, as also demonstrated by Hugo and Mauser [17].

The observed conversion rates of the complex reactions of 2-octanol and 2-octanone with nitric acids can be correlated using only two kinetic equations, in which the effect on temperature is described through the Arrhenius equation and the effect on acid strength through Hammett’s acidity function. The experimental results and simulations are in good agreement, hence the employed film model is satisfactory.
The oxidation reactions have been studied in the range 0–40°C, with initial nitric acid concentrations of 50–65 wt.% and a stirring rate of 700 rpm. The results indicate the oxidation of 2-octanol is operated in the non-enhanced regime when nitric acid is below 60 wt.% or when the temperature is below 25°C at 60 wt.% HNO₃, while the oxidation of 2-octanone is operated in the non-enhanced regime for the whole range of experimental conditions considered. Under these conditions the mass transfer resistance does not influence the overall conversion rate, so the governing parameters are the reaction rate constant and the solubility of the organic compounds in the nitric acid solution. This has also been experimentally confirmed by determining the influence on stirring rate.

Even though the kinetic constants have only been determined up to a temperature of 40°C, the simulated results for isoperibolic experiments at higher temperatures are still acceptable. Therefore it can be concluded that it has been possible to describe the thermal behavior of the semi-batch reactor for the nitric acids oxidation reactions with the film model for slow liquid–liquid reactions and a simplified reaction scheme. In a future part of this work, the thermal behavior of this consecutive heterogeneous liquid–liquid reaction system will be further evaluated.

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Appendix A. Notation

\( a \) interfacial area per volume of reactor content = \( 6\varepsilon/d₁₂ \) (m²/m³)

\( A \) effective cooling area (m²)

\( C \) concentration (kmol/m³)

\( C_p \) specific heat capacity (J/Kg K)

\( D \) diameter (m)

\( D_i \) diffusivity coefficient component \( i \) (m²/s)

\( d₁₂ \) Sauter mean drop diameter (m)

\( E_A \) enhancement factor

\( E_{Act} \) energy of activation (J/kmol)

\( h \) height (m)

\( H \) \( \Delta H \)eff,none/\( \Delta H \)eff,nol

\( H_0 \) Hammett’s acidity function

\( H_a \) Hatta number

\( J \) mole flux (kmol/m²·s)

\( k_{Laq} \) mass transfer coefficient in the aqueous phase (m/s)

\( k_{Lorg} \) mass transfer coefficient in the organic phase (m/s)

\( k_{eff} \) effective second order reaction rate constant \( \left( \text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \right) \)

\( k_{\Delta eff} \) effective preexponential constant \( \left( \text{m}^3/\text{kmol} \cdot \text{s} \right) \)

\( M \) molecular weight (kg/kmol)

\( m \) molar distribution coefficient

\( m_{H_0} \) Hammett’s coefficient

\( n \) number of moles of reactant in the reactor (kmol)

\( N \) stirring rate (s⁻¹)

\( Q \) heat flow (W)

\( R \) gas constant = 8315 (J/kmol·K)

\( r \) rate of reaction per volume of reactor content \( \left( \text{kmol/m}^3 \cdot \text{s} \right) \)

\( t \) time (s)

\( t_{dos} \) dosing time (s)

\( t_{dos} \) dimensionless dosing time, \( t/t_{dos} \)

\( \rho \) density (kg/m³)

\( \sigma \) interfacial tension (N/m)

\( \zeta_i \) conversion, \( \zeta_i = n_i/n_{A1} \)

Greek symbols

\( \alpha \) angle of cone (°)

\( \Delta H \) heat of reaction (kJ/mol)

\( \Delta E \) amount of heat (kJ)

\( \epsilon \) volume fraction dispersed phase = \( V_d/(V_d + V_c) \)

\( \phi \) flow (m³/s)

\( \Gamma \) effective heat capacity (J/K)

\( \mu \) viscosity (Ns/m³)

\( \theta \) dimensionless dosing time, \( t/t_{dos} \)

\( \rho \) density (kg/m³)

\( \sigma \) interfacial tension (N/m)

\( \zeta_i \) conversion, \( \zeta_i = n_i/n_{A1} \)

Dimensionless groups

\( Po \) Power number \( \frac{Q}{\rho_{dis}N^3D_{stir}^5} \)

\( Re \) Reynolds number \( \frac{\rho_{dis}N^2D_{stir}^2}{\mu_{dis}} \)

\( We \) Weber number \( \frac{N^2D_{stir}\rho_c}{\sigma} \)

Subscripts and superscripts

\( 0 \) initial, at \( t = 0 \)

\( 1 \) final (after dosing is completed)

\( nol \) reaction of 2-octanol, see Eq. (4)

\( none \) reaction of 2-octanone, see Eq. (5)

\( A \) component A (2-octanol)

\( Aq \) aqueous phase (nitric acid solution)

\( B \) component B (nitrosonium ion)

\( c \) continuous (aqueous) phase

\( C \) calibration

\( cool \) cooling

\( d \) dispersed (organic) phase
dispersion
dosing
effective
formation
component i
maximum
organic phase
(2-octanone)
reaction
reactor
stirring
reactor wall
component X (carboxylic acids)
(at interface)
average
ambient

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