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Kinetic modeling validation and extension for heterogeneous benzaldehyde nitration

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Highlights
- Benzaldehyde nitration kinetic model was validated under heterogeneous conditions
- Nitrobenzaldehydes were synthesized using benzyl alcohol under heterogenous conditions
- Performances of continuous and batch reactors were evaluated

1. Introduction

2- and 3- nitrobenzaldehyde are two industrial intermediates involved in the production a wide range of bulk and fine chemicals ranging from dyes, plastic additives, fragrances, and flavourings, to highly priced materials such as pharmaceuticals and innovative materials[1]. In recent investigations, an interest was shown for benzaldehyde nitration kinetic modeling in mixtures of nitric and sulfuric acid, namely mixed acid[2]. Moreover, the possibility of realizing tandem oxidation/nitration of benzyl alcohol to synthesize nitrobenzaldehydes was recently demonstrated[3]. The above investigations and modeling were carried out using an organic substrate concentration lower than its solubility in the acidic aqueous phase to realize homogeneous conditions and prevent the kinetic parameters estimation from being affected by interphase mass transfer. However, preliminary studies suggested the importance of a heterogeneous-phase reaction characterization to explain discrepancies obtained in commercially available microreactors[3]. To this regard, in this work an experimental campaign was carried out under heterogeneous conditions in batch reactors in order to extend and validate the available kinetic model. The results were compared with those obtained under homogeneous conditions and in a microreactor. Microreactors could be an attractive alternative to safely carry out hazardous reactions such as highly exothermal tandem oxidations and nitrations.

2. Methods

Ternary aqueous mixtures of mixed acid were prepared by drop-wise addition of the acids to water under continuous stirring and cooling. A proper volume of nitrating mixture was added in a batch jacketed glass reactor (20 mL) and preheated to operating temperature. For each experimental run a proper volume of organic substrate was added at once to the nitrating mixture (total volume = 1 mL) under continuous stirring. The reaction was quenched by dilution (1:10) adding 9 mL of a cold solution of urea in acetonitrile (4 g/L). The resulting homogeneous solution was further diluted (1:100) and submitted to HPLC analysis. The continuous flow experiments were run in a commercial glassmicroreactor with embedded mixer and heat exchanger (Little Things Factory XXXL-ST-04).Solubility evaluations were made adding an amount of organic to the reaction media at fixed temperature under continuous mixing for 6 hours. The aqueous phase was thus separated, diluted and analyzed.HPLC analysis was performed using an Agilent 1100 HPLC, a UV DAD detector, and a PhenomenexSynergi 4 μmpolar RP/80A column. The mobilephase (1.0 mL/min) was constituted of eluent (A) (buffersolution: CH_3OH 5% v/v; H_3PO_4 0.4% v/v; H_2O 94.6% v/v) and eluent (B) (acetonitrile). The signals were acquired atwavelength of 210, 230, 250, and 265 nm.

3. Results and discussion

Solubilities of the main formed organic species during benzaldehyde nitrations, i.e. benzaldehyde (Be), 2-nitrobenzaldehyde (2NBe) and 3-nitrobenzaldehyde (3NBe), were measured in mixed acid at varying temperature and composition. As a general result, solubilities were found to increase with temperature and acids concentrations. Specifically, the logarithm of the molar fraction of organics in aqueous mixed acid was

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found to linearly increase with 1/T, where T is the absolute temperature in K. Moreover, linear and parabolic semi-empirical correlations were found to describe the solubilities of the organic compounds at varying acids concentrationin the neighborhood of standard mixed acid composition, i.e. 20 % wt. HNO_3 and 60 % wt. H_2SO_4, normally employed in organic substrates nitrations. Experimental batch runs were carried out in kinetic regime. The assumption was verified, demonstrating that the kinetics were independent on the magnetic stirrer speed. The previous published kinetic models[2-3] were thus modified as follows

$$\frac{dn_i}{dt} = \sum_j (\pm)k \cdot n_j^{aq} \tag{1}$$

$$V_{aq} = V_{aq}^0 + V_{org}^{diss} \tag{2}$$

where (1) takes into account the contribution of formation (positive) or consume (negative) of the organic species i and where n_j^{aq} is the number of moles of the species j dissolved in the organic phase where the reaction takes place. The solubility and the volume of the aqueous phase change during the reaction as nitric acid is being consumed while water is being formed. The experimental results were simulated without any further adjustment of the previous estimated kinetic parameters, showing a good agreement (Fig. 1). Similar results were obtained when starting from benzyl alcohol instead of benzaldehyde.
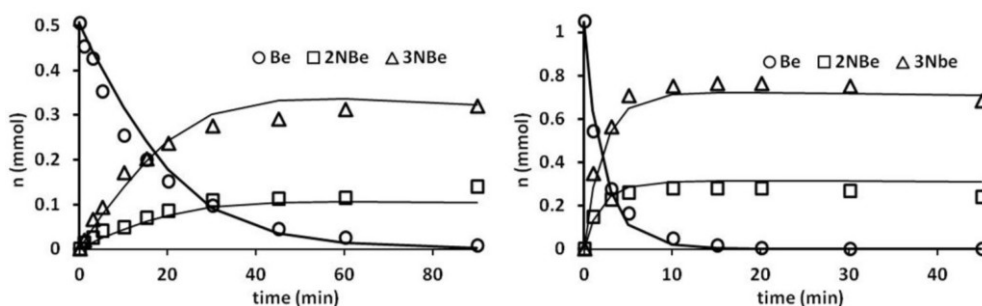

Figure 1. Benzaldehyde nitration under heterogeneous conditions. Simulated (continuous lines) and experimental (symbols) data.

Experimental runs carried out in a microreactor showed similar results in terms of products partition. However, under heterogeneous continuous flow, kinetic regime cannot be assumed and benzaldehyde conversions was always lower than those obtained in batch at the same residence time. However, the conversion resulted to be higher when adopting higher flow rates, confirming the influence of the mass transfer on the conversion. As an example, in 20 % wt. HNO_3 and 64 % wt. H_2SO_4 at 35 °C, a 95% conversion was achieved after 10 min in batch, whereas 66% and 79% conversions were achieved in the microreactor for flow rates of 0.3 and 0.45 mL/min, respectively.

4. Conclusions

The previously estimated kinetic parameters for benzaldehyde nitration and tandem oxidation/nitration of benzyl alcohol were used to extend the kinetic model to heterogeneous systems. The adoption of a microreactor enabled to safely carry out the reactions. Even though the conversion in microreactors was lower than in a lab-scale batch reactor, it must be considered that it could be significantly higher than in a scaled-up batch reactor, in which the kinetic regime is rarely achieved.

References

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