

Nitric Acid Decomposition Kinetics in Mixed Acid and their Use in the Modelling of Aromatic Nitration

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Nitric acid decomposition in mixed acid (an aqueous mixture of nitric and sulfuric acids) was studied from a chemical and a kinetic point of view. The study was focused on the behavior of the reactive mixture in an open system in which the gas formed through the decomposition process can leave the vessel. The reaction network, through which the system could develop, depending on the chemical composition of the mixture and on the temperature, was completely characterized. The data collected indicate that water evaporation can significantly influence the system behavior. Isothermal experiments were carried out to estimate the unknown kinetic parameters through the adoption of a mathematical model able to predict the system behavior at varying process conditions. The proposed model and the estimated parameters were validated through the use of the results collected in a set of experimental runs performed during the nitration of methyl m-nitrobenzoate (3NMB) in mixed acid media.

1. Introduction

Nitration processes are widely carried out on an industrial scale since nitrated products have extensive applications, directly or as intermediates, in chemical industry (Olah et al, 1989). Although a certain number of these reactions have already been widely studied in the past (Robinson et al, 1932), there are still some unclear points about the mechanism and the kinetics of the nitration process; hence the interest in studying them from theoretical and practical points of view. The most common nitrating system currently adopted on industrial scale, is the classic mixed acid ($\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) (Olah et al, 1989). It is well known in the literature that nitric acid undergoes thermal decomposition in strong acidic medium (Ballod et al, 1989; Copelli et al, 2013) and similar indications were reported also for mixed acid. However, despite its extensive use, up today there are no literature indications on the kinetic parameters of nitric acid decomposition during nitration and the network involved. Moreover, runaway phenomena, which take place when the thermal control of the process is lost, could occur during nitration processes due to the system exothermicity as a result of side reactions such as polynitration and/or decomposition (Di Somma et al, 2012; Andreozzi et al, 2005). On the basis of these considerations, nitric acid decomposition in mixed acid (an aqueous mixture of nitric and sulfuric acids) was studied from a chemical and a kinetic point of view. The study was focused on the behavior of the reactive mixture in an open system in which the gas formed through the decomposition process can leave the vessel.

2. Material and methods

2.1 Nitric acid decomposition

A series of sealed, open, stirred glass tubes of $1.45 \cdot 10^{-2}$ L total volume was filled with $1.0 \cdot 10^{-4}$ L of mixed acid (nitric and sulfuric acids) at a fixed composition, previously prepared in isothermal mode at 290 K. During the runs, in order to obtain isothermal conditions the test tubes were placed into an oil bath at a desired temperature between 320 and 350 K and their thermal behavior was recorded. After the desired reaction time, the samples were withdrawn from the oil bath, rapidly cooled and submitted to an acid-base

titration to know the total acid (the sum of the moles of nitric and sulphuric acid) concentration in the system.

2.2 Nitration process

A jacketed glass magnetically stirred (volume: $3.0 \cdot 10^{-2}$ L) reactor was used. The temperature was kept at the desired value by using a Julabo F32 refrigerated/heating circulator. For each run to a proper volumes ($1.0 \cdot 10^{-2}$ - $2.0 \cdot 10^{-2}$ L) of mixed acid with specific composition previously prepared an amount of organic substrate (methyl m-nitrobenzoate, 3NMB) was instantaneously added. Each sample withdrawn from the reactor at varying reaction times was chemically quenched by means of a dilution in methanol. The concentration of the organic species involved, as a function of reaction time, was determined by HPLC analysis using a Hewlett-Packard model 1100 II, equipped with an UV-VIS detector and a Phenomenex Synergi 4 μ polar RP/80A column.

3. Results and discussion

During a previous investigation (Di Somma et al, 2012), a safety assessment for the nitration process of methyl benzoate had been performed and, in particular, the kinetic behavior of methyl m-nitrobenzoate - the target product of the methyl benzoate nitration- in mixed acid solutions in a closed system had been investigated. Unfortunately, the previous model failed when it was used to predict the chemical behavior of a reactive open system in which the concentrations of the components (such as nitric acid, sulfuric acid and water) were different from those used to obtain it. In fact, when the kinetic parameters identified were used to simulate the data collected during 3NMB nitration performed in an open system starting from more concentrated mixtures than those previously used, the results obtained were unsatisfactory (Figure 1).

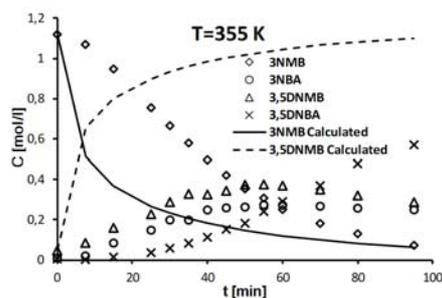


Figure 1: Comparison between experimental (symbols) and calculated (continuous and dot lines).

In other words, the system behaved as if there was an amount of nitric acid lower than that actually charged in the reactor. On the basis of these results, it was clear that other reactions involving nitric acid were occurring under the conditions adopted, which the previous model did not account for. Hence a set of isothermal experiments, at varying reaction temperatures and mixed acid composition, was performed. Some results are shown Figure 2.

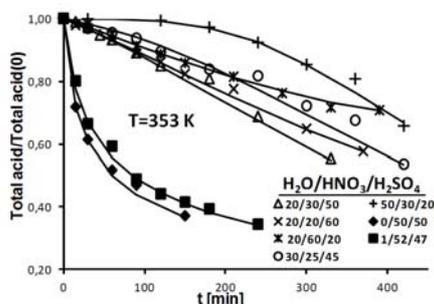


Figure 2: Total acid decay at different mixture composition: Reaction temperature = 353 K. Comparison between experimental (symbols) and calculated (continuous lines) results.

It is possible to observe that nitric acid decomposition rate rises when H₂O decreases; in fact, in the run performed with the largest water percentage (cross), not only is the reactivity recorded the lowest ever obtained during the experimental campaign but a change in the concavity of the curve is observed vs. all the other runs. On the other hand, during the run performed in total absence of water (X), the maximum system reactivity is observed. To analyze the effect of mixture composition on system reactivity a proper variable was identified :

$$\frac{n_{HNO_3} \cdot n_{H_2SO_4}}{n_{H_2O}} \quad (1)$$

where n_i is the number of moles of i -th component. To verify the capability of this variable to explain the different reactivities recorded during the experimental campaign, for each run shown in Figure 2, the slope of the line approximating the curves around time zero was calculated and reported versus the initial value of the variable (see Figure 3).

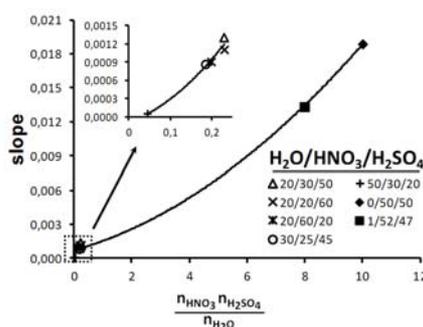
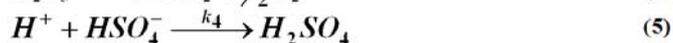
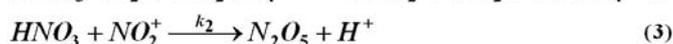
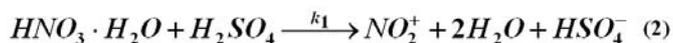


Figure 3: Interpolating lines slope of the runs reported in Figure 2 versus the selected variable.

From the results obtained, it is possible to state that there is a relationship between the reactivity of the system and the variable selected, the higher the value of the latter the higher the reactivity itself.

3.1 Kinetic assessment

The results reported and discussed in the previous paragraphs indicate the possibility that the total acid concentration decreases in concentrated mixed acid and in open system at temperatures significantly higher than ambient values. From a literature survey it was found that, despite nitration processes are commonly used in the chemical industry, there are no kinetic indications on this phenomenon. On the basis of the results reported above it can be hypothesized that the decomposition rate directly depends on the product between the initial moles of nitric and sulfuric acids and that is negatively affected by the total amount of water added to the system, too. On the basis of these considerations, a reaction network for the process of the decomposition of nitric/sulfuric acids mixture in open systems was proposed and reported in Scheme 1.



Scheme 1.

In particular, if the reaction reported in the Eq (4) is very fast, some gaseous products rapidly form. These products (NO₂ and O₂), along with the water initially present or formed during the process, leave the reactor the system being open and the temperature being significantly higher than ambient values. Therefore, the reaction (2) cannot reach an equilibrium condition. On the basis of the reactions reported in

Scheme 1, a mathematical model aiming at describing the system behavior was developed. For each species included in Scheme 1, a material balance equation was written, in particular in the water material balance, the contribution of the evaporation is taken into account based on the film theory by means of the following term:

$$\theta = \frac{Kc \cdot S}{R \cdot T} \cdot x_{H_2O} \cdot \gamma_{H_2O} \cdot P_{H_2O}^0 \quad (6)$$

Where Kc and S are the specific surface and the mass transfer coefficient respectively.

The activity coefficients γ were calculated through the Wilson equations (Zaldivar et al, 1992); the molar volume v of the i -th species and the total volume were evaluated according to literature indications (Khudhair et al, 1989).

The experimental results obtained during all the runs, at varying initial conditions, were simultaneously used in a single optimization procedure (Di Somma et al, 2011) to estimate the unknown kinetic parameters $A_1, E_1, A_2, E_2, A_4, E_4$, introduced in the scheme 1, and the coefficient Ka defined as:

$$Kc \cdot S = a' \cdot D^{2/3} \cdot S = K_a \cdot D^{2/3} \quad (7)$$

In which D is water diffusivity.

The estimated values of the unknown parameters are reported in Table 1 and some examples of comparison of calculated and experimental concentrations are shown in Fig.2.

Table 1: Best estimated values for the parameters reported in Scheme1

Reaction	A_n [cm ³ /(min·mmol)]	E_n [kcal/mol]	Ka [cm ³ /min]
1	$4.7 \cdot 10^{(4 \pm 0.30)}$	10.7 ± 0.4	$7.0 \cdot 10^{-(1 \pm 0.05)}$
2	$4.5 \cdot 10^{(4 \pm 0.22)}$	20.1 ± 0.6	
3	$1.0 \cdot 10^{(5 \pm 0.35)}$	20.0 ± 0.5	

3.2 Upgrading of the nitration model

The following step of the investigation was testing the model for nitric acid decomposition during the nitration runs performed on the 3NMB according to the procedure reported in the experimental section (2.2). To do so, it was necessary to combine the two reaction networks, the first describing the nitric acid decomposition in the mixed acid in open systems at temperatures higher than ambient values (scheme 1) and the second describing the nitration of 3NMB (Figure 4). It is important to highlight that, differently from what proposed in the kinetic scheme reported elsewhere (Di Somma et al, 2012), to model the nitration process of nitrobenzoate in the present situation, the reaction (eq. 2) cannot be considered as an equilibrium. In fact, in the previous investigation, the experimental runs were performed in closed system in which the gases that formed and water were unable to leave the vessel.

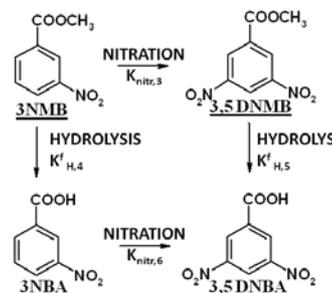


Figure 4: Reaction scheme for 3NMB nitration.

On the basis of this scheme it is possible to write the complete set of differential equations describing the evolution of the reactive system (not reported). Five unknown parameters were present in the set of differential equations reported above ($A_{\text{nitr},3}$, $E_{\text{nitr},3}$, $A_{\text{nitr},6}$, $E_{\text{nitr},6}$ (see scheme 2) and $Kc \cdot S$ (mass transfer coefficient multiplied for specific surface)) and were evaluated by the same optimization procedure previously described and using experimental results collected during two nitration runs of 3NMB for which the previous model (Di Somma et al, 2012) had failed (see Fig.1). The comparison between the calculated data and the experimental ones are shown in Figure 5 whereas the best estimated values for the unknown parameters are listed in Table 2.

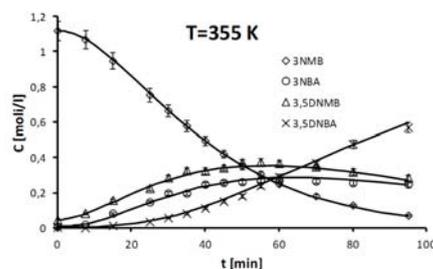


Figure 5: Comparison between experimental (symbols) and calculated (continuous lines) data for methyl *m*-nitrobenzoate nitration, at 353 K and in an open system.

Table 2: Best estimated values for the unknown parameters describing the reaction process

Nitration reaction	$A_{\text{nitr},i}$ [l/(min·mol)]	$E_{\text{nitr},i}$ [kcal/mol]	$Kc \cdot S$ [l/min]
3	$8.9 \cdot 10^{(6 \pm 0.07)}$	15.7 ± 1.10	2.2 ± 0.01
6	$4.6 \cdot 10^{(3 \pm 0.04)}$	10.5 ± 0.6	

3.3. The validation of the proposed model

To validate the proposed model, an additional nitration run was performed on 3NMB in an open system. In this run, even if the coolant was kept at constant temperature (357 K), while loading the mixed acid (previously formed and kept at 357 K) in the vessel containing the organic substrate, the mixing heat caused an instantaneous temperature increase. To model this behavior, since the mixing heat was unknown “a priori” and due to the very fast nature of this process, the starting temperature was assumed as equal to the maximum value attained (400 K) after loading the mixed acid. On the basis of this consideration, a thermal balance equation was added to the above set of differential equations. The complete system of differential equations describing the investigated system was solved with the appropriate initial conditions without any adjustment of the parameters. The results obtained are reported in Figure 6. It is possible to state that the new model is able to well predict the system behavior.

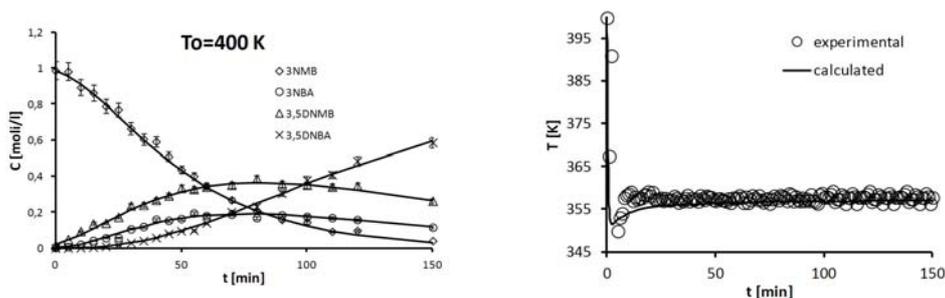


Figure6: Comparison between experimental and calculated data for methyl *m*-nitrobenzoate nitration in mixed acid, at 400 K, in an open system and in isoperibolic conditions.

4. Conclusions

The decomposition of nitric acid in mixed acid and in an open system has been studied from a kinetic point of view. The results obtained have been used to develop a mathematical model able to describe the system behavior at varying operating conditions. The model has been also used to simulate the kinetic behavior of the system methyl *m*-nitrobenzoate/mixed acid. To do so a previous model has been upgraded, which has required the evaluation of new kinetic parameters. Satisfactory results have been obtained in a validation procedure of the estimated kinetic parameters, which have been used to simulate the data collected during additional nitration experiments performed under operating conditions different from those used to develop the model.

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