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Nitric acid decomposition kinetics in mixed acid and their use in the modeling of aromatic nitration

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HIGHLIGHTS

- A kinetic characterization of nitric acid decomposition in mixed acid is achieved.
- The decomposition arises in an open system from which formed gases may escape.
- The nitration of 3-nitrobenzoate in an open system has been modeled.
- A thermal balance equation has been included in the developed model.
- The target nitration carried out under isoperibolic batch mode has been simulated.

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ABSTRACT

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 application, directly or as intermediates, in the chemical industry for example as dyes, explosives, pesticides and drugs [1,2]. Although a certain number of these reactions have already been widely studied in the past [3,4], 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 an industrial scale, is the classic mixed acid ($HNO_3/H_2SO_4/H_2O$) [5]. It is well known in the literature that nitric acid undergoes thermal decomposition in strong acidic medium [6] and similar indications were reported also for mixed acid [7]. However, despite its extensive use, as at today there is no literature 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 [8,9], could occur during nitration processes as a result of system exothermicity and of side reactions such as polynitration and/or decomposition. With respect to this aspect, it is useful to remark that nitrations are, along with polymerizations [10] and oxidations [11], among the most dangerous reactions at industrial level also for the inherent thermal instability of the products [12,13]. On the basis of these considerations, a chemical and kinetic characterization of the reaction network through which the investigated system (the mixed acid plus the organic species) develops in case of uncorrected feed of the mixture or undesired temperature increase, was carried out. The investigations herein were performed in an open system to take into account the possibility that the gas formed by the process can leave the vessel along with the water evaporated. The ultimate goal of this work is the collection of all the information necessary to build a complete kinetic model able to simulate the behavior of the reactive system during a nitration process [14] under different operating conditions.

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Nomenclature

m_S	sample mass (g)
ΔH_i	heat of *i*th reaction (J g^{-1})
C_{pi}	i-th sample specific heat (J g^{-1} K^{-1})
ϕ	thermal inertia (dimensionless)
C_R	vessel thermal capacity (J K^{-1})
T	temperature (K)
R	universal constant of gas (J mol^{-1} K^{-1})
k_n	kinetic constant for *n*th reaction (L mol^{-1} min^{-1})
r_n	velocity of *n*th reaction (mol L^{-1} min^{-1})
A_n	pre-exponential factor for *n*th reaction (L mol^{-1} min^{-1})
E_n	activation energy for *n*th reaction (kJ mol^{-1})
t	reaction time min
a_i	activity of *i*th species (mol L^{-1})
γ_i	activity coefficient of *i*th species (dimensionless)
n_i	moles of *i*th species (mol)
k_R^f	gross kinetic constant for *R*th reaction (L^2 mol^{-2} min^{-1}) or (min^{-1})
E_R^f	gross activation energy for *R*th reaction (kJ mol^{-1})
k_{0R}^f	gross pre-exponential factor for *R*th reaction (L^2 mol^{-2} - min^{-1}) or (min^{-1})
y_i	calculated concentration of *i*th species (mol L^{-1})
C_i	concentration of *i*th species (mol L^{-1})
x_i	molar fraction of *i*th species (dimensionless)
v_i	molar volume of *i*th species (L mol^{-1})
P_i^0	vapor pressure of *i*th species (atm)
M_i	molecular weight of *i*th species (g mol^{-1})
K_c	mass transfer coefficient (cm min^{-1})
S	exchange area (cm^2)
D	diffusivity (cm^2 min^{-1})
U	global heat transfer coefficient (J cm^{-2} min^{-1})
$\Delta S_{(j)}$	entropy change for the *j*th equilibrium (J K^{-1} mol^{-1})
$\Delta H_{(j)}^0$	enthalpy change for the *j*th equilibrium (J mol^{-1})
λ_{vap}	heat of evaporation (J mol^{-1})

2. Material and methods

2.1. Nitric acid decomposition

A series of sealed, open, stirred glass tubes of 1.45×10^{-2} L total volume was filled with 1.0×10^{-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 checked by means of a small thermocouple in contact with the solution and connected to an appropriate system developed using LabView to acquire and process temperature data. After the desired reaction time, the samples were withdrawn from the oil bath, rapidly cooled and submitted to an acid–base titration [15] to know the total acid (the sum of the moles of nitric and sulfuric acid) concentration in the system.

2.2. Nitration process

A jacketed glass magnetically stirred (volume: 3.0×10^{-2} L) reactor was used. The temperature was kept at the desired value by using a Julabo F32 refrigerated/heating circulator (cooling fluid: water). The thermal behavior was checked by means of a thermocouple in contact with the solution and connected to an appropriate acquisition system. All the runs were carried out in batch mode. For each run proper volumes (1.0×10^{-2}–2.0×10^{-2} L) of mixed acid with specific composition were prepared by adding, dropwise, a desired amount of bidistilled water and, successively, of nitric acid to sulfuric acid under cooling (283–293 K). After the increase in temperature up to a desired value, an amount of organic substrate (methyl m-nitrobenzoate, 3NMB) was instantaneously added to the solution. Each sample was chemically quenched by means of a dilution in methanol (1.0×10^{-4} L of each sample withdrawn from the reactor at varying reaction times were rapidly diluted in 1.0×10^{-2} L). 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. During the preliminary tuning of all the experimental procedures, the HPLC analysis was repeated at different times on the same solution kept at room temperature to check that no changes happened in the concentration of the species analyzed. For the mobile phase, a mixture of 70% of a buffer solution (vol%: CH_3OH 5%, H_3PO_4 0.4%, H_2O 94.6%) and 30% of acetonitrile was used with a flow rate of 1×10^{-3} - L min^{-1}. The signals were acquired at 210, 220, 230 and 240 nm. The column temperature was set up at 298 K. For all the experiments analytical grade reagents were used (H_2SO_4 was obtained from Fluka and the other reagents from Sigma Aldrich).

All the runs were carried out twice and the analysis on a single samples three times. The data on the diagrams were reported as a mean value with the relative standard deviation (error bars).

3. Results and discussion

During a previous investigation [16], 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 [17,18] – 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

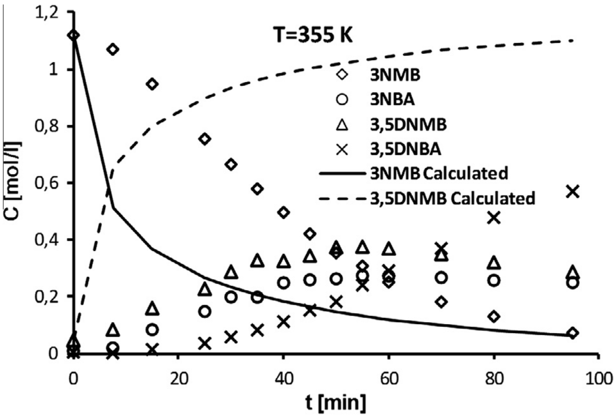

Fig. 1. Comparison between experimental (symbols) and calculated (continuous and dot lines) data for methyl m-nitrobenzoate nitration in mixed acid, at 355 K and in an open system. Initial system concentrations: C_{3NMB} = 1.12 mol/L, $C_{HNO_3} = 11.05$ mol/L, $C_{H_2SO_4} = 6.36$ mol/L, $C_{H_2O} = 0.94$ mol/L. Initial mixed acid composition (% weight/weight): HNO_3 = 52.02%, H_2SO_4 = 46.75%, H_2O = 1.23%. 3NMB = methyl m-nitrobenzoate; 3NBA = 3-nitrobenzoic acid; 3,5DNMB = 3,5-dinitro methyl benzoate; and 3,5DNBA = 3,5-dinitrobenzoic acid.