



## Chemical kinetic model for methylurea nitrosation reaction: Computer-aided solutions to inverse and direct problems



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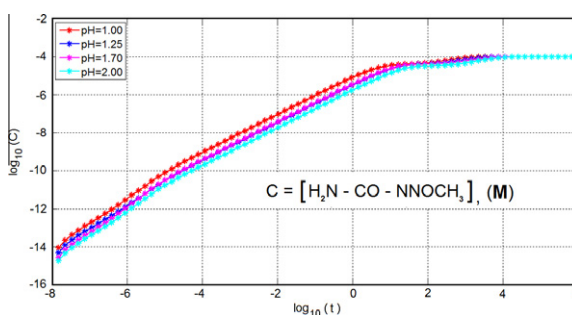
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### HIGHLIGHTS

- ▶ A kinetic model was built based on proposed mechanism of methylurea nitrosation.
- ▶ The model represents a system of ordinary differential equations of stiff type.
- ▶ The optimization of rate constants has been accomplished using genetic algorithm.
- ▶ The direct problem has been solved revealing the histories of all chemical species.
- ▶ The kinetic model has been validated statistically using analysis of variance.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this work, a kinetic model consisting of eight-step reactions has been constructed to simulate the mechanism of the nitrosation reaction of methylurea. The model represents a system of ordinary differential equations (ODEs) of stiff type. Firstly, for establishing the initial conditions of nitrosation, an equilibrium model for nitrite ions has been developed and solved numerically. Secondly, the inverse problem of nitrosation reaction kinetics has been addressed in order to optimize the rate constants. In this respect, stiff ODEs have been integrated numerically using Rosenbrock method, and the parameters (rates constants) have been optimized by genetic algorithm (GA). The optimization of rate constants has been performed by fitting the model outputs with available experimental data. Both the model prediction and the experimental results show a good agreement, with a maximum deviation error of 8.5%. In addition, the kinetic model has been validated statistically using the analysis of variation (ANOVA). The computed optimal rate constants depend on pH of the medium of reaction. Lastly, by solving the direct problem it has been possible to trace the reaction via simulation, to provide insight and to gain information about histories of all species (i.e.  $\text{NO}^+$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2^-$ ,  $\text{HNO}_2$ , methylurea and N-nitroso-N-methylurea) participating into the nitrosation process under different pH conditions. Model simulations have demonstrated that for the proposed mechanism the significant role is attributed to  $\text{N}_2\text{O}_3$ ,  $\text{NO}^+$  and  $\text{HNO}_2$  in the first moments of reaction, i.e. for  $t < 10^2$  s, while  $\text{NO}_2^-$  has shown the most important role after that ( $t > 10^2$  s). The results of computation also suggested that higher pH values slowed down the rate of formation of nitrosamine (i.e. N-nitroso-N-methylurea).

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## Nomenclature

ARE	average relative error (performance function of fitting)	$t_F$	final reaction time
$C$	concentration (dependent variable)	$\Delta t$	integration step-size
$D$	mesh size (number of integration steps)	$x_1$	initial concentration of nitric acid
$DF$	degree of freedom	$x_2$	equilibrium concentration of dinitrogen trioxide
$f$	function	$x_3$	equilibrium concentration of nitrosonium ions
$h$	initial concentration of hydrogen cations	[ ]	square brackets meaning the concentration of chemical species embedded in
h	hour		
$k$	rate constant of a step reaction		
$\mathbf{k}$	chromosome (vector of reaction rate constants)		
$K$	equilibrium constant of a reversible reaction	<i>Subscripts and superscripts</i>	
$L$	number of model parameters	$A, B, C$	indexes of the reversible reactions
$m$	initial concentration of nitrite anions	$a, b$	indexes of the step reactions
$M$	molarity or molar concentration (mol/l)	$e$	equilibrium
MSE	mean-square-error (fitness function)	$exp$	experimental value
$\mu$	number of decision variables	$calc$	calculated (theoretical) value by means of the model
$N$	number of data points (experimental trials)	$i$	iteration index (integer value)
$N_T$	total number of data points (comprise all series of experimental trials)	$j$	mesh index (integer value)
$p$	integer positive number	$l$	integer index
$r$	rate of reaction	$n$	index of reaction (integer value)
$q$	number of individuals (population size) in GA	$T$	transpose operator for vector and matrix
$s$	second	$t_0$	denote initial time for ODEs – model
$T$	temperature	$u$	integer index
$t$	reaction time (independent variable)	#	denote selected individuals (parents) in genetic algorithm
$t_0$	initial reaction time	0	denote initial condition
		*	denote the optimal value of rate constant

## 1. Introduction

In the last decades, the biogeochemical cycle of nitrogen in nature has been strongly affected by the pollution with nitrates, nitrites and nitrosamines. Nitrosamines are the chemical compounds of environmental concern since they belong to the class of dangerous chemicals that has been shown to be carcinogenic, mutagenic and teratogenic [1–3]. The US Environmental Protection Agency (US EPA) has placed these compounds into the Group B2, defined as the probable human carcinogen substances [2]. Owing to the high carcinogenic activity of nitrosamines, their maximum permissible concentrations are usually set at the low levels of order of  $10^{-6}$  mg/L [2–5].

Nitrosamines have been identified in the surface and ground waters [3,6], drinking waters [7–9], waste-waters [10,11], soils [12,13], foodstuffs [14,15], tobacco products and cigarette smoke [16,17]. In addition, the formation of nitroso compounds can occur under acid conditions in the digestive tract (especially in the stomach). To avoid the presence of nitrosamines in the environment it is necessary to prevent their formation by understanding how they are generated [3]. It is well known that nitrosamines are formed by nitrosation reactions, for instance, nitrite reacts with amines, amides and amino acids to form N-nitroso compounds [18]. Furthermore, the carcinogenic nitrosamines such as N-nitrosodimethylamine (NDMA) can be formed in the process of water disinfection, from the reactions of chlorine or chloramines with dissolved dimethylamine or natural organic matter [3].

Until now, the most published papers on the subject of nitrosamines mainly dealt with their qualitative and quantitative analysis; inhibition and removal of nitrosamines from the environment as well as the assessment of their toxicity. In contrast, few papers have been addressed to the mathematical modeling and computational simulation of the nitrosation process.

In order to minimize the formation of nitrosamines it is necessary to assess their rates of formation. In this respect, the chemical

kinetic modeling and analysis is very essential. The role of a chemical kinetic model is to predict the evolution of the concentrations with time for each chemical species of the system under investigation. Such kinetic model is very useful for the prediction of concentrations evolution, especially for the species that are difficult to detect experimentally. The aim of kinetic analysis is to build a model describing all simple chemical reactions occurred within the system, based on molecular kinetics [19].

Licht and Deen reported a theoretical model for predicting the rates of nitrosamine and nitrosamide formation in the human stomach [20]. In that work, the authors proposed a mathematical model developed to estimate the rates of formation of nitrosamines and nitrosamides in the human stomach, under a variety of physiological and environmental conditions. The proposed model combines a detailed description of the kinetics of N-nitrosation with mass balance equations, which account for gastric emptying, dilution and absorption. The simulations were carried out considering the variations in gastric pH. A comparison of the theoretical results with available experimental data on the nitrosation process suggested that the model had predicted accurately the rates of nitrosamine formation [20].

Lewis and co-workers [21] have studied the kinetics of N-nitrosation of morpholine in oxygenated nitric oxide solutions at physiological pH. It was shown that phosphate and chloride ions were capable of inhibiting N-nitrosation of morpholine. In addition, Caulfield et al. [22] have reported similar inhibitory effect of N-nitrosation using bicarbonate.

Kharitonov and collaborators [23] investigated the kinetics of nitrosation of thiols by nitric oxide in the presence of oxygen revealing that the reaction rate constants of the nitrosating species with thiols were in the range of  $1.5\text{--}3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

Garcia-Santos et al. [24,25] estimated the reactivity of amino acids in nitrosation reactions revealing that the main nitrosating agent was dinitrogen trioxide ( $\text{N}_2\text{O}_3$ ) and that the nitrosation rate was proportional to the square of nitrite concentration. An

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