

* Corresponding author: gslopes@ufc.br

Electronic Supplementary Material

Study of the chemical kinetic of TVG-IR system

The application of the integrated rate laws for Hg^{2+} and CH_3Hg^+ was unsuccessful when trying to fit the experimental data to a zero, first or second order reaction (Figures 1 and 2). It can be seen that the rate of reduction accelerates as the reaction proceeds, possibly indicating multiple order, a sequential process with different reductants/intermediates, or a varying concentration of a key reactant. It was not possible to adapt the data obtained to a second order (Figure 1 (c) and 2 (c)), even though this could be a possible second order reaction in the initial stage (possible adaptation of the data to a linear fit), these data from the initial period were used to plot the graph shown in Figure 1 (d) and 2 (d) separately, not being possible to adjust this to a linear fit. The inability to achieve a first order (Figure 1 (b)) adequate to the data suggests that the thermal decomposition products of formic acid may promote a subsequent secondary reduction of Hg^{2+} and, in this case, the kinetics of the reaction may also be influenced by the formation of reducing intermediates such as $\cdot\text{H}$, CO , $\cdot\text{HCOO}$ or $\cdot\text{HCO}$ formed during the thermal decomposition process of formic acid.²²

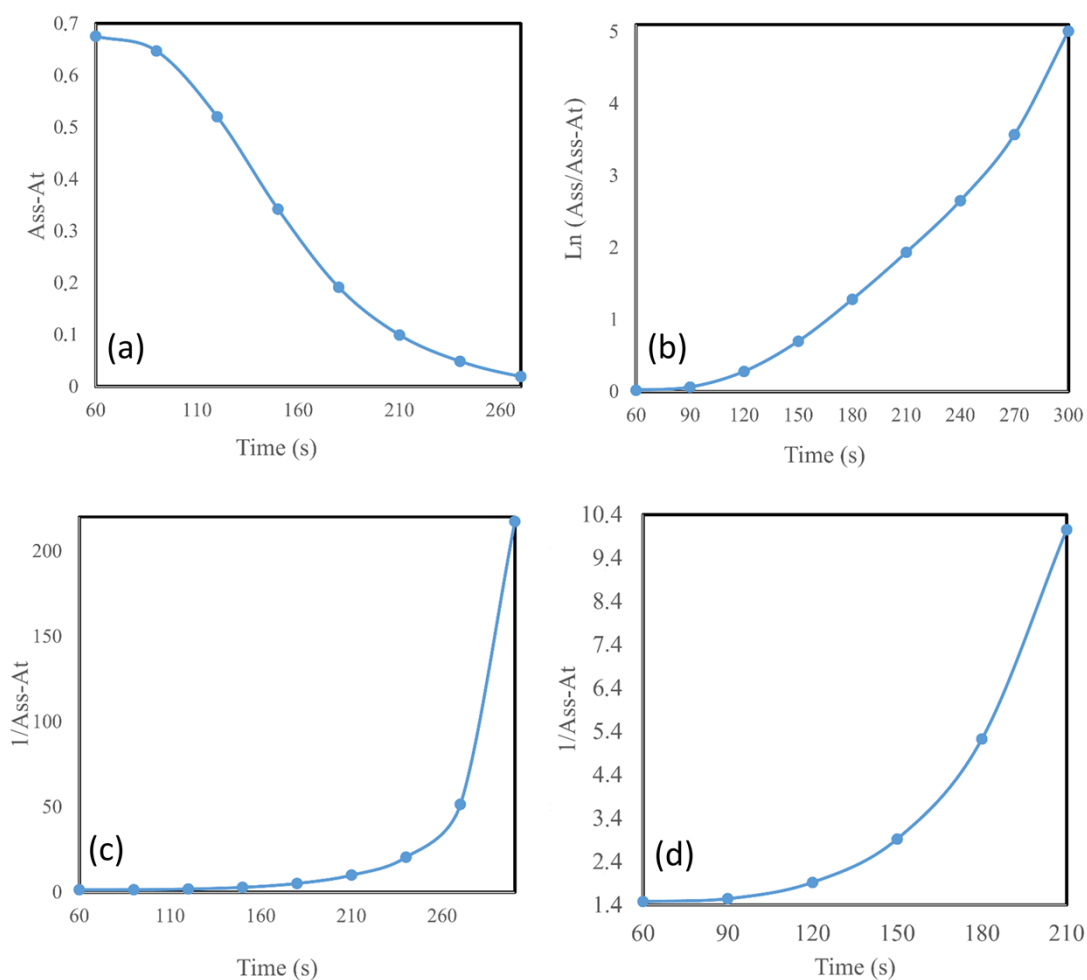


Figure 1. Fitting data for a $20 \mu\text{g L}^{-1}$ of Hg^{2+} reduction in 2% formic acid using TVG-IR to (a) zero-order kinetic plot; (b) first order; (c) second order in the interval from 60 to 300s and (d) second order in the interval from 60 to 210s. Note, for convenience: Ass = Absorbance measured in the period of the steady state signal, At = Absorbance measured in the t (time period).

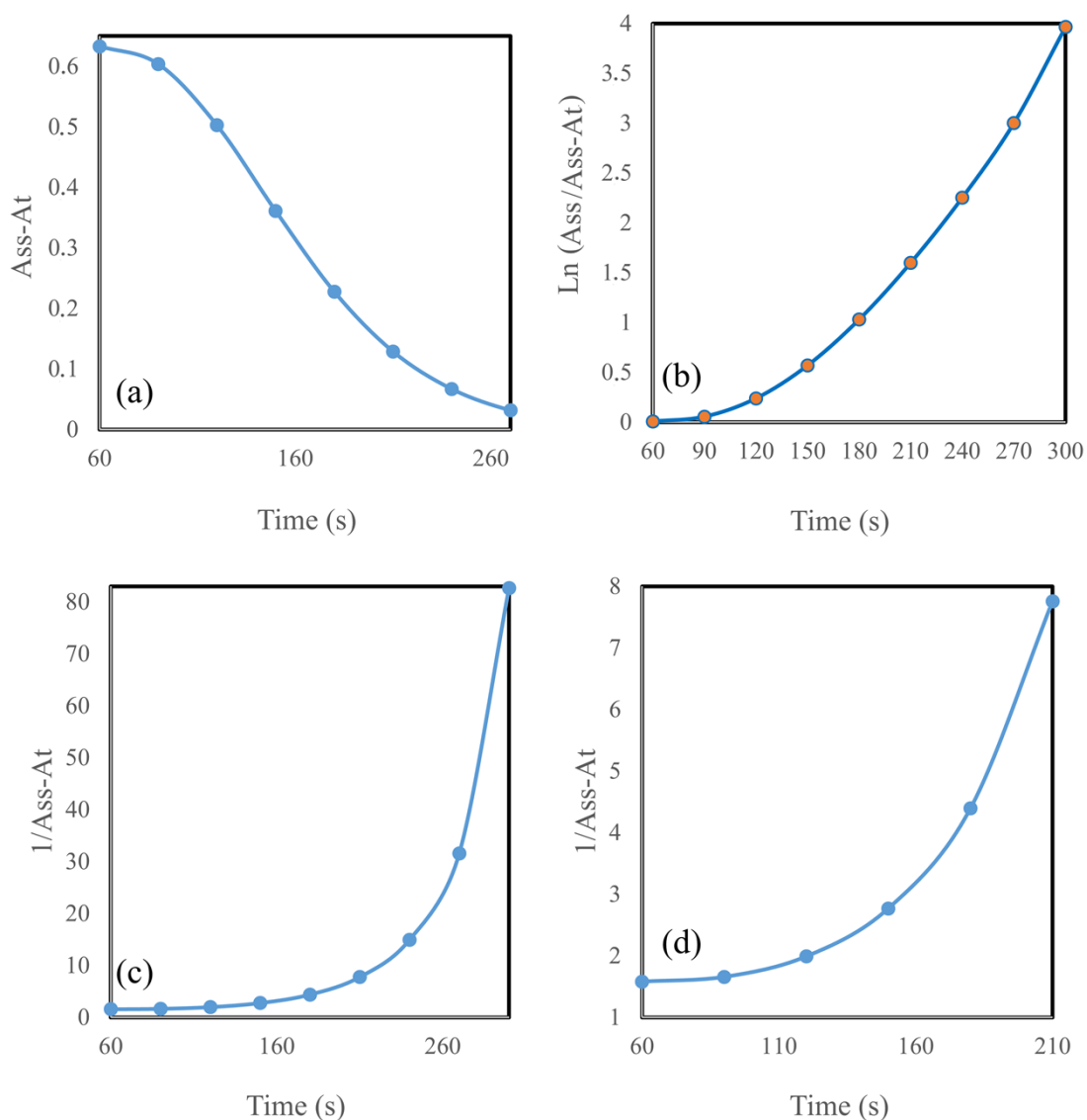


Figure 2. Fitting data for a $20 \mu\text{g L}^{-1}$ of Hg^{2+} reduction in 2% formic acid and hydrogen peroxide $0.25\% \text{ v v}^{-1}$ using TVG-IR to (a) zero-order kinetic plot; (b) first order; (c) second order in the interval from 60 to 300s and (d) second order in the interval from 60 to 210s (d). Note, for convenience: Ass = Absorbance measured in the period of the steady state signal, At = Absorbance measured in the t (time period).

Sturgeon and Luong⁸ investigated the kinetic profile of the thermochemical generation of mercury vapor by conductive heating in an oil bath at $87.4 \text{ }^\circ\text{C}$, and observed that

the variation of the formic acid concentration in the range of 2 to 8% had no perceptible impact on the format of the integrated response curve. The response curves obtained by the authors could be readily fitted to a pseudo-first-order integrated rate equation. In this system, complete reduction (As-s) occurred in 8 minutes. For comparative purposes, the authors also performed reduction reactions in an oil bath of 82 °C that revealed first-order kinetics for Hg^{2+} .