

## Supplementary Material

### Inverse solvent effects in the heterogeneous and homogeneous epoxidation of *cis*-2-heptene with [2-percarboxyethyl]-functionalized silica and *meta*-chloroperbenzoic acid

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**General.** Solvents and reagents were purified before use by following standard procedures.<sup>1</sup> Glassware was successively washed with an aqueous EDTA solution (0.125 g L<sup>-1</sup>), ultrapure water and acetone purified by distillation from KMnO<sub>4</sub>. Peroxydic reagents **1** were stored at 3°C in the dark. The GC analyses were performed with a capillary column Agilent HP1 (30 m length, internal diameter 0.32 mm and film thickness 0.25 μm), with an injector temperature of 250°C and FID temperature 280 °C.

[2-Pericarboxyethyl]-functionalized silica (**1a**) was prepared by the sol-gel method following reported procedures.<sup>2,3</sup> Prior to each kinetic experiment, solid peracid **1a** was dried under vacuum (0.01 mm Hg) at room temperature until it reached a constant weight, and its peroxydic content was determined by standard iodometric titration. *meta*-Chloroperbenzoic acid (*m*CPBA) (**1b**) 96-99% w/w was obtained by treating commercial samples (60-70%) with a K<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffer solution at pH 7.5 and at room temperature for 6 h, followed by recrystallization at -20 °C from *n*-hexane/diethyl ether 3:1. The *m*CPBA solutions (**1b**) (0.05 M) in the different solvents were prepared at the same temperature of the experiments using a thermostatted bath. The peroxydic content of the solution was determined prior to each kinetic experiment.

Solutions of *cis*-2-heptene (0.01 M) and adamantane, as an internal standard (0.005 M), in the different solvents (Table 1) were prepared at the kinetic experiment temperature with a thermostatted bath. The reaction conditions for each kinetic experiment were previously optimized for each peracid and solvent, and depended mainly on the boiling point of the solvent and the solubility of *m*CPBA (**1b**) in each case. The kinetic experiments were performed at least three times for each solvent and temperature.

**Kinetic experiments for 1a. General procedure.** To a solution (4 mL) of *cis*-2-heptene (0.01 M) and adamantane (0.005 M), as an internal standard in dichloromethane, placed in a jacketed flask thermostatted at  $20.0 \pm 0.1$  °C by a recirculating bath, solid peracid **1a** (0.4 mmol) was added at once under stirring (400 rpm). The aliquots (0.2 mL) withdrawn from the reaction mixture were quenched with 0.4 mL of a 0.25 M solution of thioanisole in dichloromethane, filtered through a Teflon syringe filter (0.2 µm) and analyzed by gas chromatography. Substrate conversions were determined from the ratio of peak areas *cis*-2-heptene/adamantane found for the starting solution and the corresponding aliquot.

**Kinetic experiments for 1b. General procedure.** To a solution (2.5 mL) of *cis*-2-heptene (0.01 M) and adamantane (0.005 M), as an internal standard in dichloromethane, placed in a jacketed flask thermostatted at  $20.0 \pm 0.1$  °C by a recirculating bath, a 0.05 M solution of *m*CPBA (**1b**) (5 mL, 0.25 mmol) in the same solvent, thermostatted at the same temperature, was added under stirring (400 rpm). The aliquots (0.4 mL) withdrawn from the reaction mixture were quenched with 0.1 mL of a 1 M solution of thioanisole in dichloromethane, and were analyzed by gas chromatography. Substrate conversions were determined from the ratio of peak areas *cis*-2-heptene/adamantane found for the starting solution and the corresponding aliquot.

Figures S1-22 show the *pseudofirst* order plots  $\ln ([olefin]_t/[olefin]_0)$  versus time obtained for the epoxidations of *cis*-2-hexene with [2-percarboxyethyl]-functionalized silica (**1a**) and *meta*-chloroperbenzoic acid (**1b**) in *n*-hexane, carbon tetrachloride, dichloromethane, chloroform and acetonitrile at 20.0 °C, and in *n*-hexane, dichloromethane and chloroform at 30.0/39.6 °C, -10.0/5.0 °C, and 10.0/35.0 °C, respectively. Figures S23-28 show the temperature dependence of the rate constants for the reactions of **1a** and **1b** with *cis*-2-hexene in chloroform (10.0/20.0/35.0 °C), dichloromethane (-10.0/5.0/20.0 °C) and *n*-hexane (20.0/30.0/39.6 °C). Activation parameters were calculated from these plots by applying the following equations.<sup>[4]</sup>

$$k = A \cdot \exp [E_a / RT]$$

$$\Delta H^\ddagger = E_a - RT$$

$$\Delta S^\ddagger = R \cdot \ln A - R \ln (\kappa T / h) - R$$

## References

- 1 D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd Edition, Pergamon, New York, 1988.
- 2 J. A. Elings, R. Ait-Meddour, J. H. Clark, D. J. Macquarrie, *Chem. Commun.* **1998**, 2707-2708.
- 3 a) R. Mello, A. Alcalde-Aragonés, A. Olmos, M. E. González-Núñez, G. Asensio *J. Org. Chem.* **2012**, *77*, 4706-4710. b) R. Mello, A. Alcalde-Aragonés, M. E. González-Núñez, G. Asensio *J. Org. Chem.* **2012**, *77*, 6409-6413.
- 4 K. A. Connors, *Chemical Kinetics. The Study of Reaction Rates in Solution*. VCH, Weinheim, 1990.

Figure S1

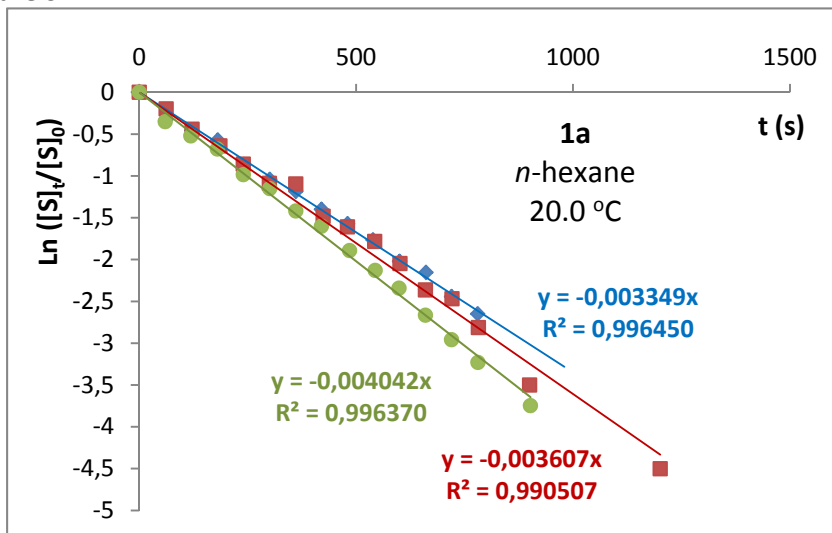


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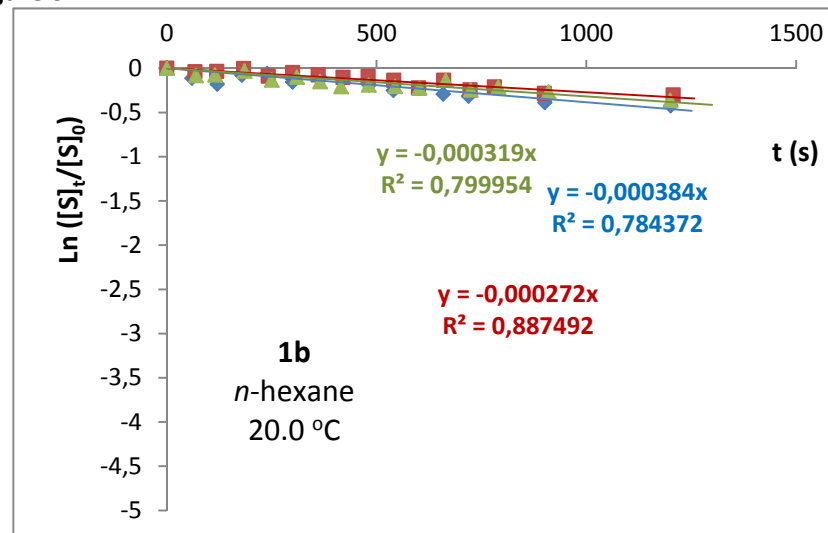


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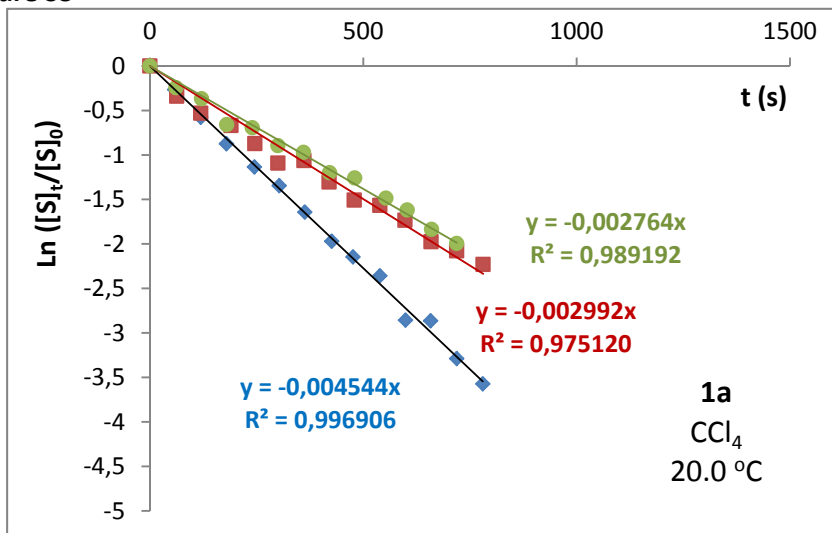


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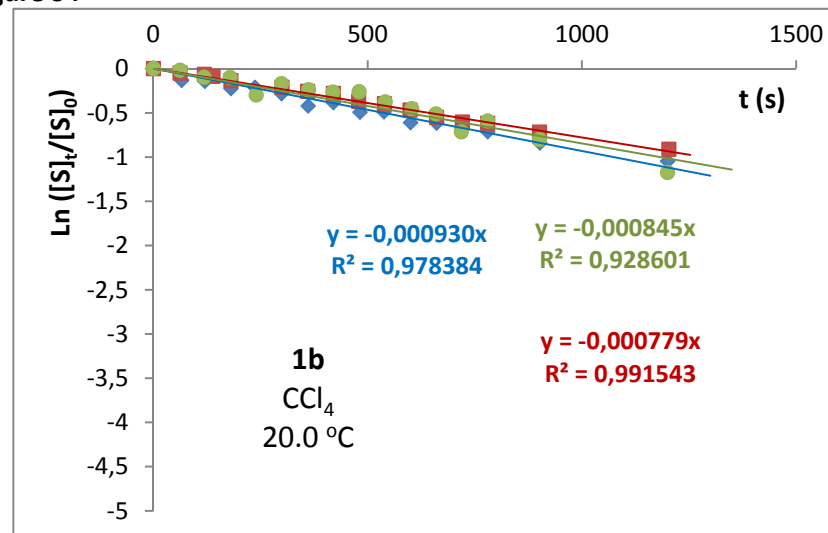


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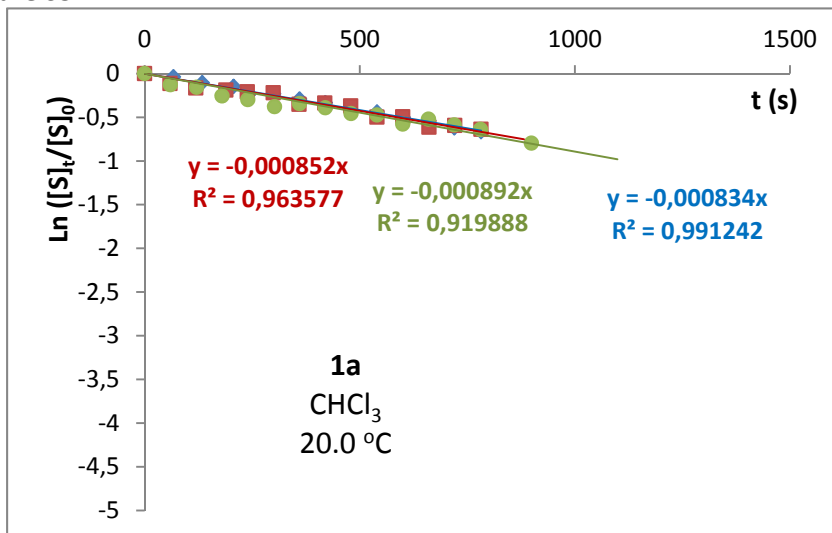


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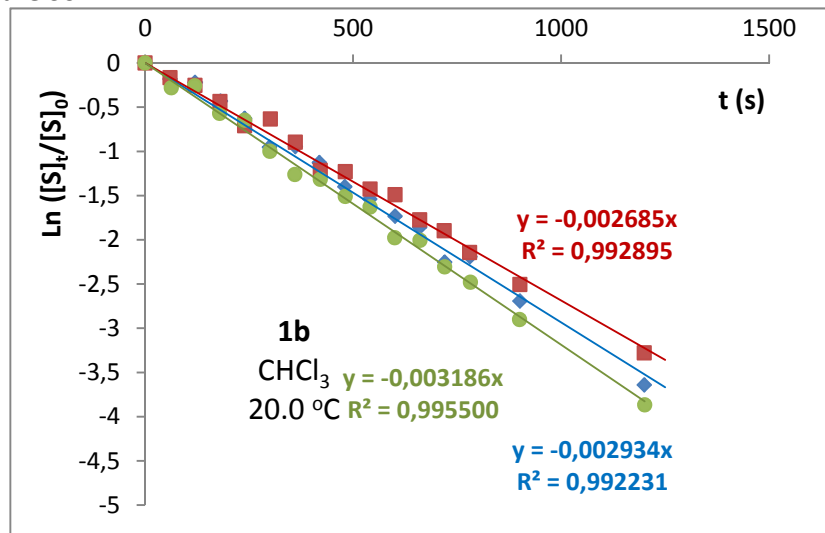


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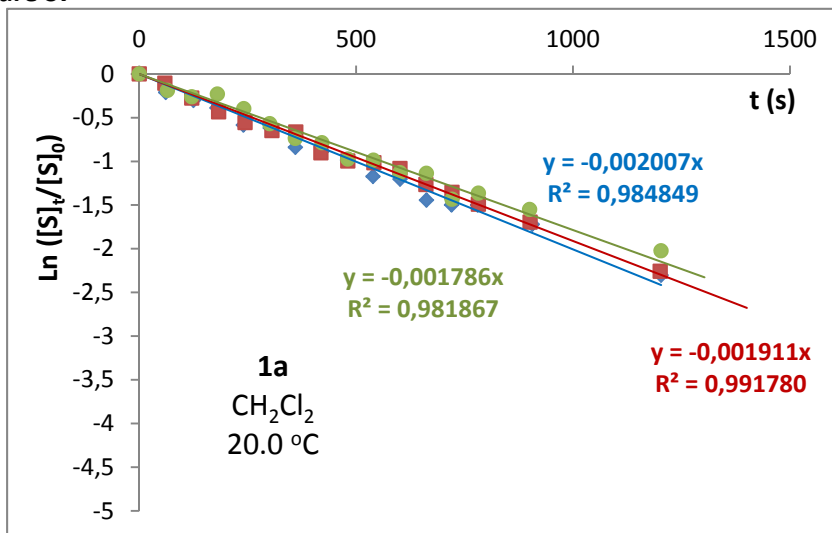


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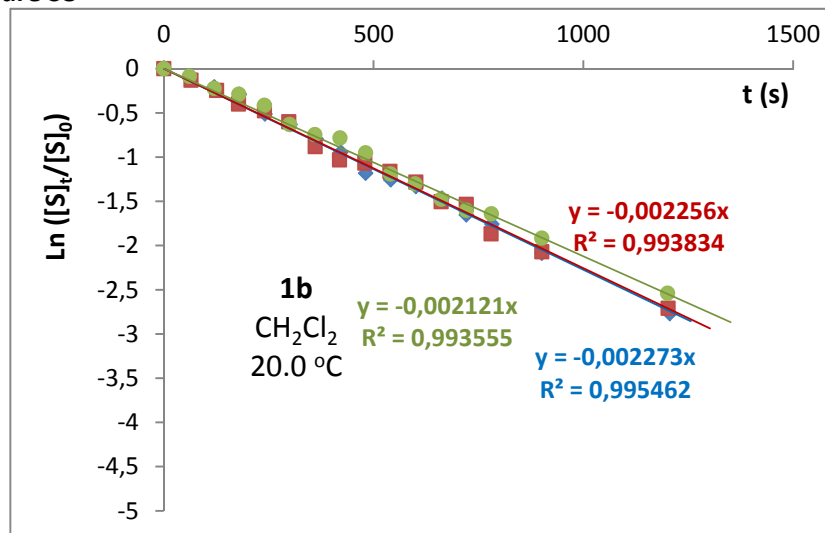


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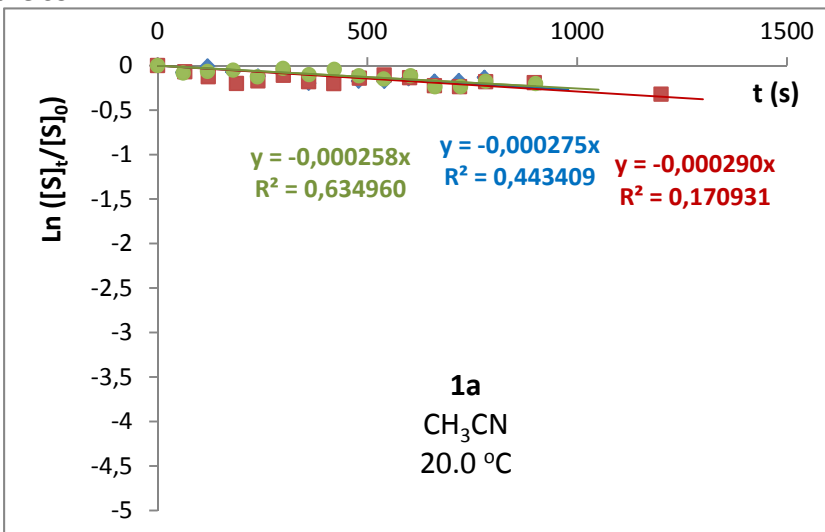


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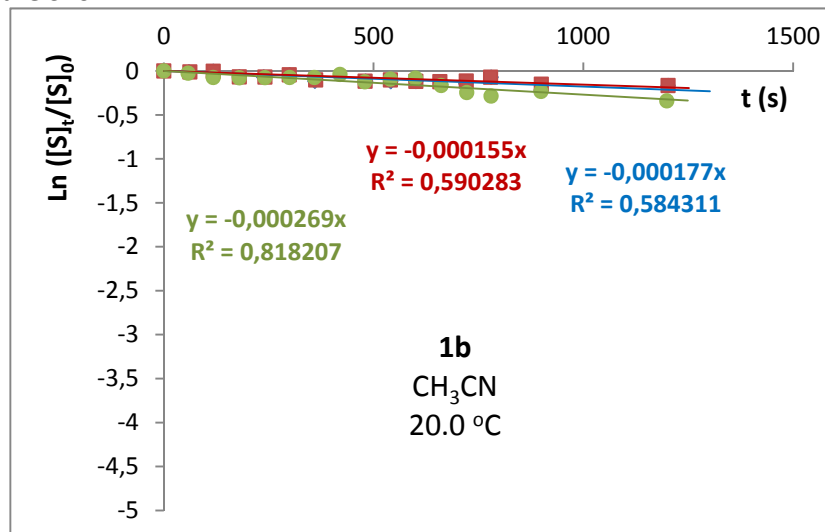


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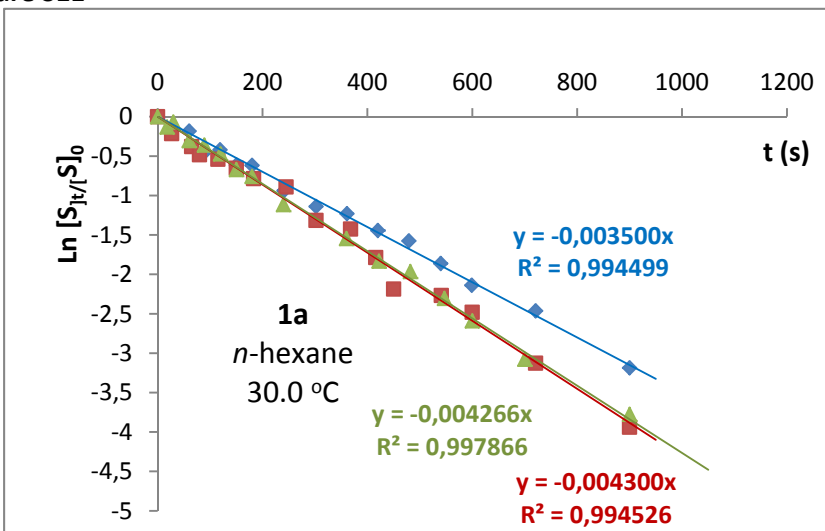


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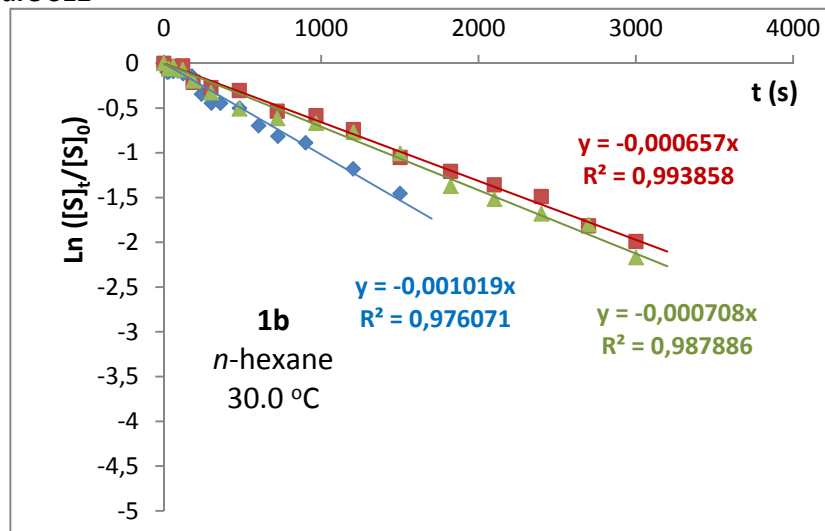


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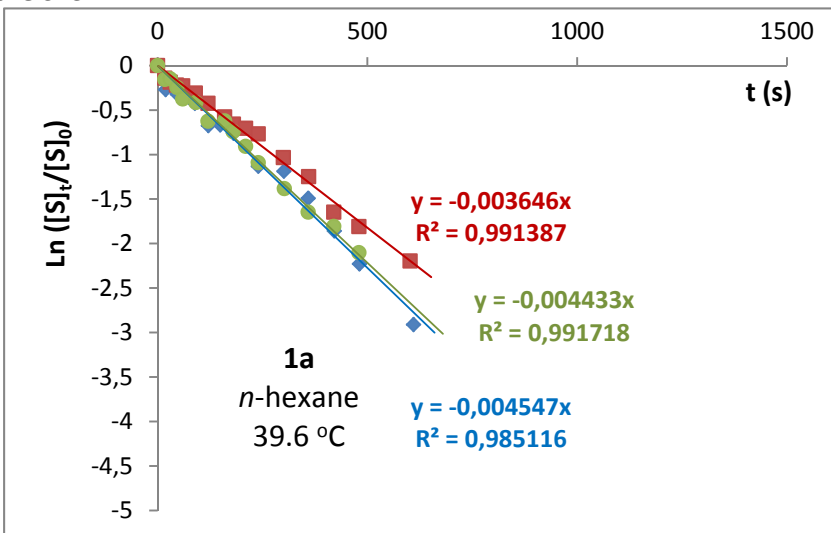


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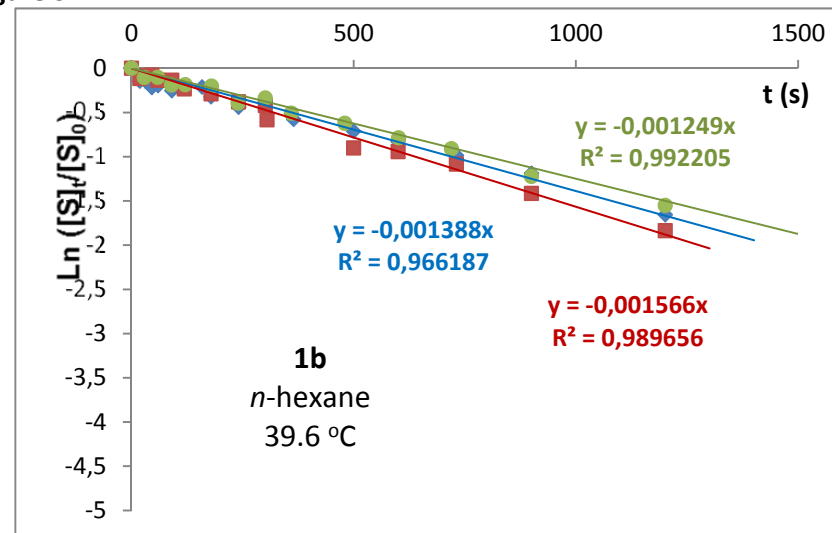


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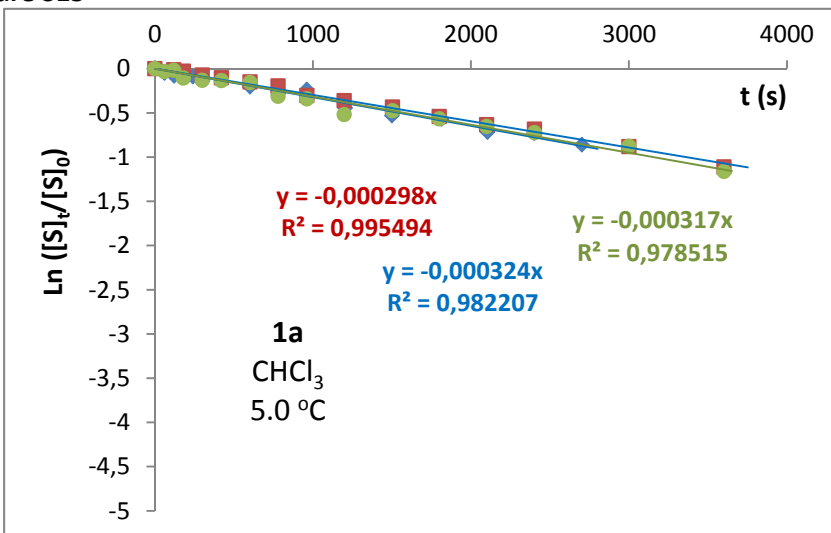


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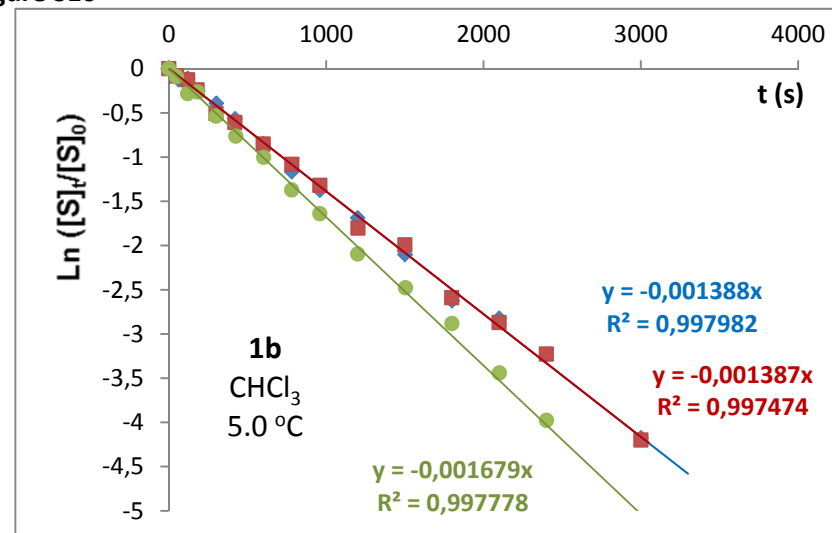


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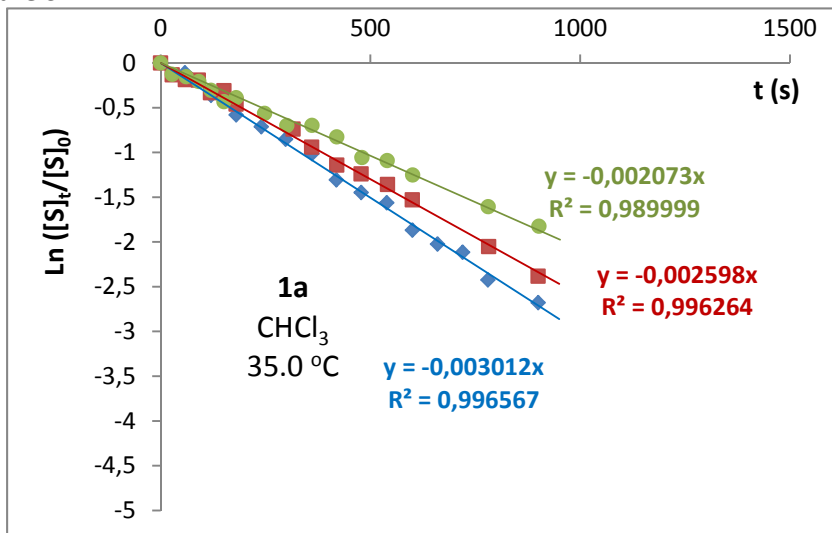


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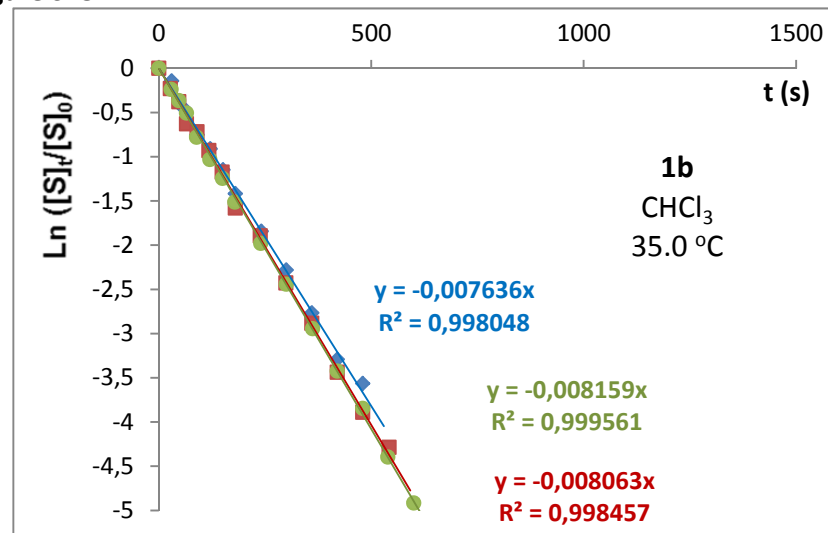


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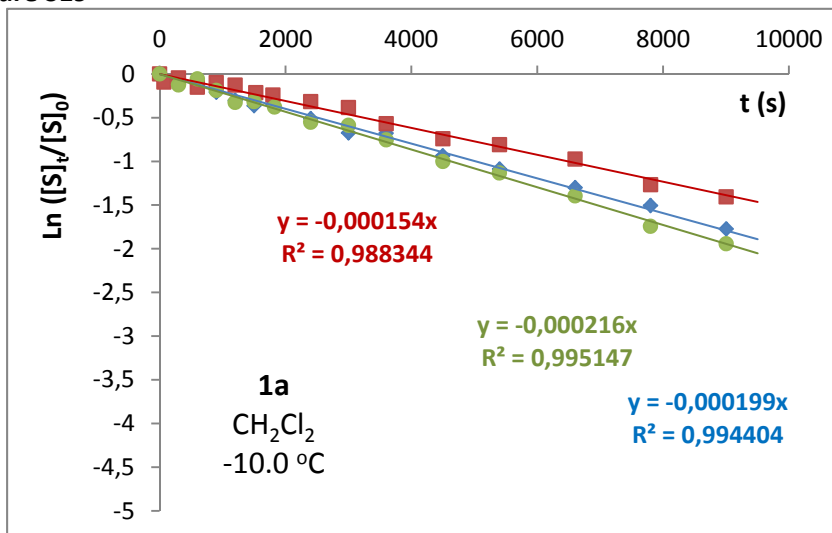


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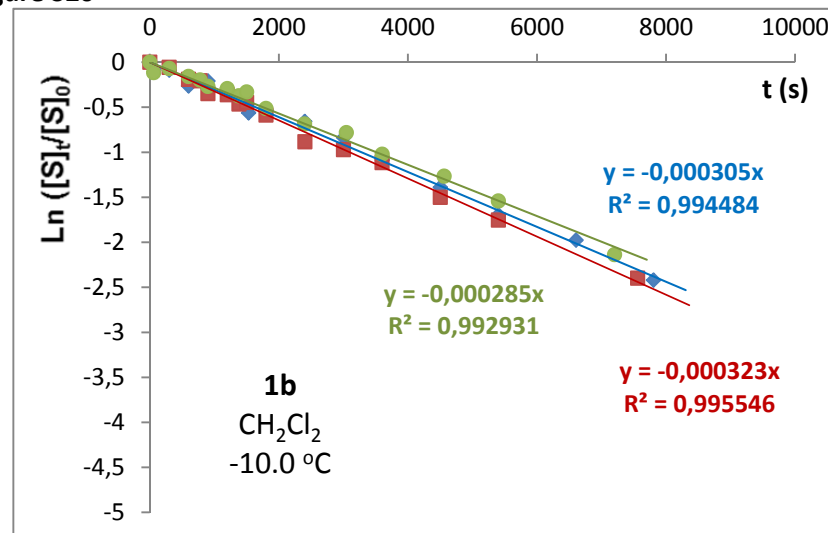


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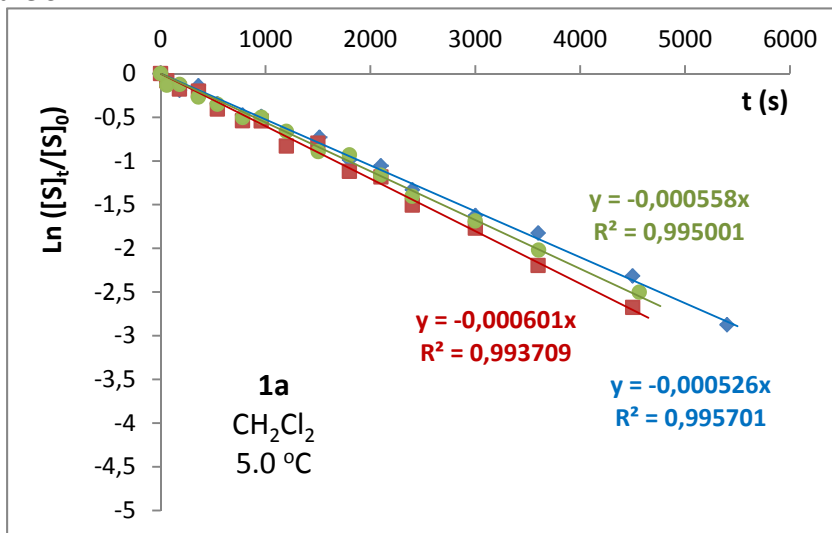


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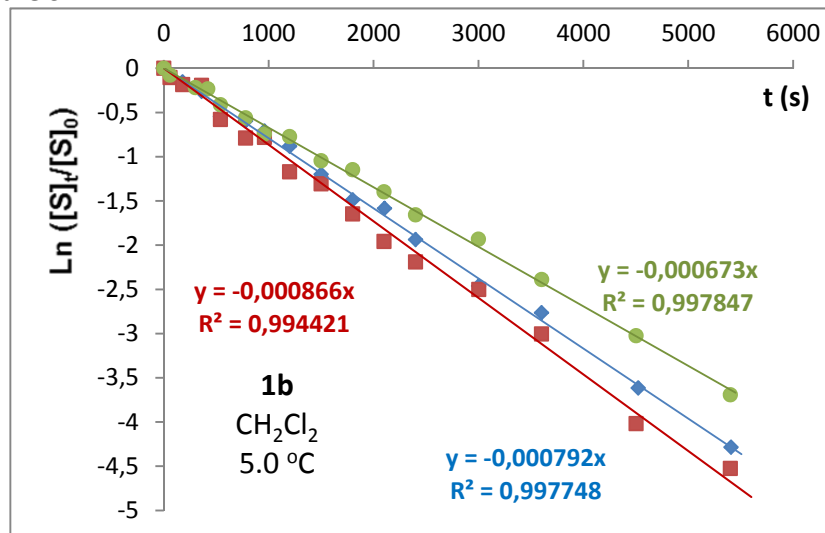


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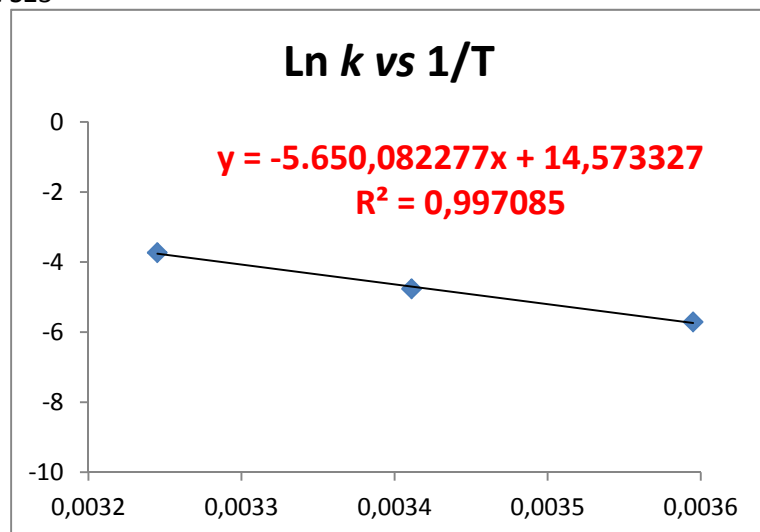


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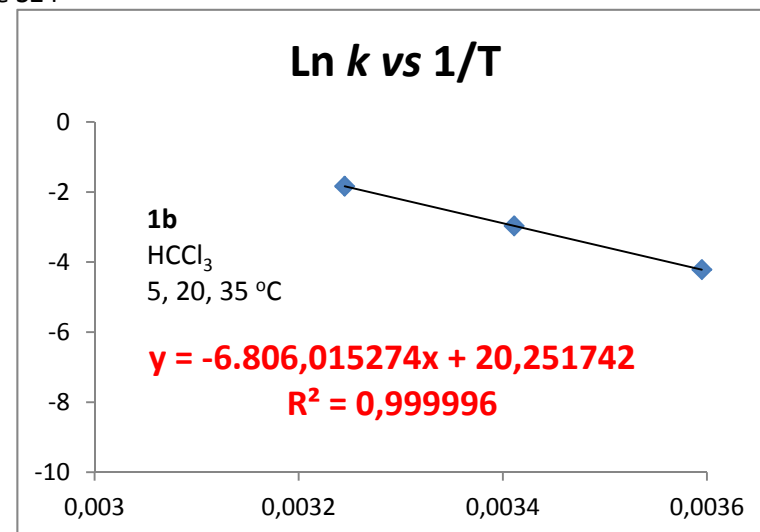




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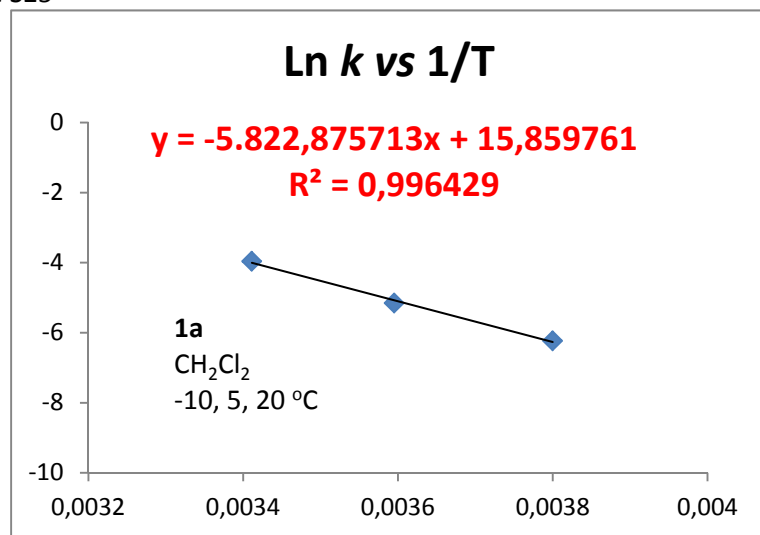


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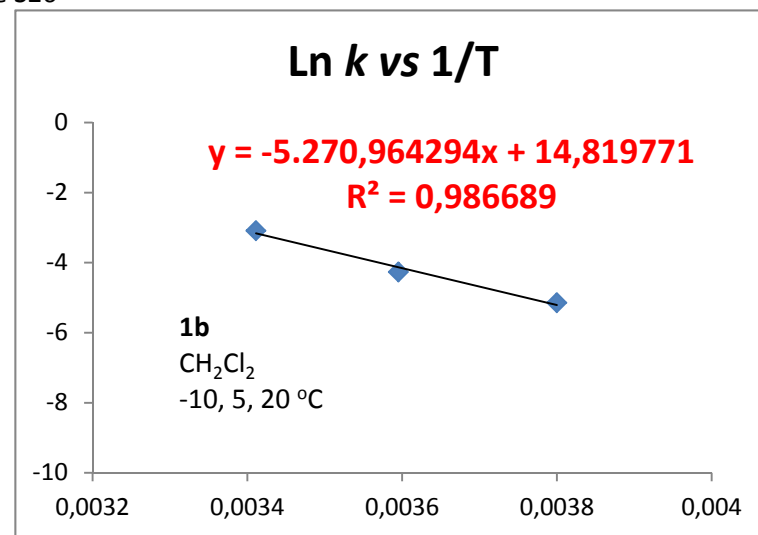


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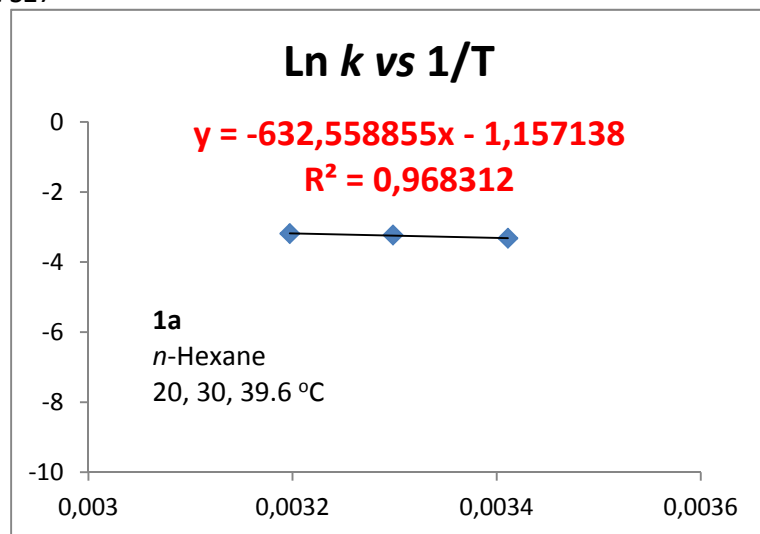


Figure S28

