

# The feasibility of using carbamates to track the thermal state in geothermal reservoirs



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## ABSTRACT

Organic compounds with functional groups susceptible to hydrolysis hold the potential to become thermo-sensitive tracers. To broaden the range of available compound classes for typical temperatures encountered in low enthalpy geothermal reservoirs, the group of carbamates was investigated. The kinetic parameters of eight primary and one secondary carbamate(s) were studied by means of isothermal batch experiments. The influence of several parameters on hydrolysis kinetics was investigated, which included the compound structure, temperature, and pH/pOH. The results demonstrate the possible application of these tracers within a broad range of temperatures.

## 1. Introduction

An important aspect of sustainable development is the availability of renewable energy resources (Dincer, 2000), and among these resources, geothermal energy carries a significant potential in the near future (Fridleifsson, 2001; Lund and Boyd, 2016). To optimize the long-term operation of geothermal reservoirs, proper exploitation strategies must be applied. Reinjection is a common technique in geothermal reservoir management that plays an important role in influencing the success of a geothermal reservoir (Kaya et al., 2011). However, the utilization of this method may lead to the risk of early thermal breakthrough (Stefansson, 1997); therefore, it generally requires the monitoring of the reservoir's spatial and temporal temperature distribution. In the past decades, the application of tracers with thermo-sensitive properties to track the thermal state of a geothermal reservoir has been demonstrated as a promising tool in both laboratory (Maier et al., 2015a,b) and field scale research (Adams and Davis, 1991; Hawkins et al., 2017; Rose and Clausen, 2014). A recent promoted approach to track the thermal distribution involves the use of hydrolysable compounds with known kinetic properties, such as esters and amides (Maier et al., 2015b; Nottebohm et al., 2012; Schaffer et al., 2016). These compounds are derived from common conservative dye tracers (e.g., naphthalene sulfonates) in which a reactive group susceptible to a well-defined thermo-sensitive hydrolysis reaction is incorporated.

Depending on the underlying decay mechanism, thermo-sensitive

tracer compounds potentially cover a wide range of temperatures (e.g., Adams and Davis, 1991; Nottebohm et al., 2012; Rose et al., 1999; Schaffer et al., 2016). In particular, amides hold great potential for exploitation within the temperature range of 100–200 °C. Furthermore, the hydrolysis reaction of amides is rather independent from environmental pH/pOH conditions, and the reaction products have a high thermal stability (Schaffer et al., 2016). For temperatures lower than 100 °C, esters are proposed as good tracers to track thermal changes (Nottebohm et al., 2012). However, esters are likely to be unstable in a reservoir in which the hydrolysis reaction may be catalyzed (e.g., by microbial activity (Gianfreda and Rao, 2004; Hawkins et al., 2017)) and consequently accelerated, making these compounds unfavorable for field applications. On the contrary, carbamates are more stable due to the donation of the nitrogen's free electron pair to the carbonyl group (resonance stabilization) (Larson and Weber, 1994). Additionally, carbamates are more electrophilic than amides due to the presence of an additional electronegative oxygen atom, which may facilitate faster hydrolysis for carbamates than amides.

To extend the number of applicable compounds for tracking geothermal temperatures, various carbamates (eight primary and one secondary) were investigated. A similar approach to that of Schaffer et al. (2016) was applied to examine the influence of the molecule structure, temperature, and pH/pOH on the hydrolysis kinetics of carbamates. The aim of this study is to widen the current knowledge of thermo-sensitive tracers and to progress towards the designing of

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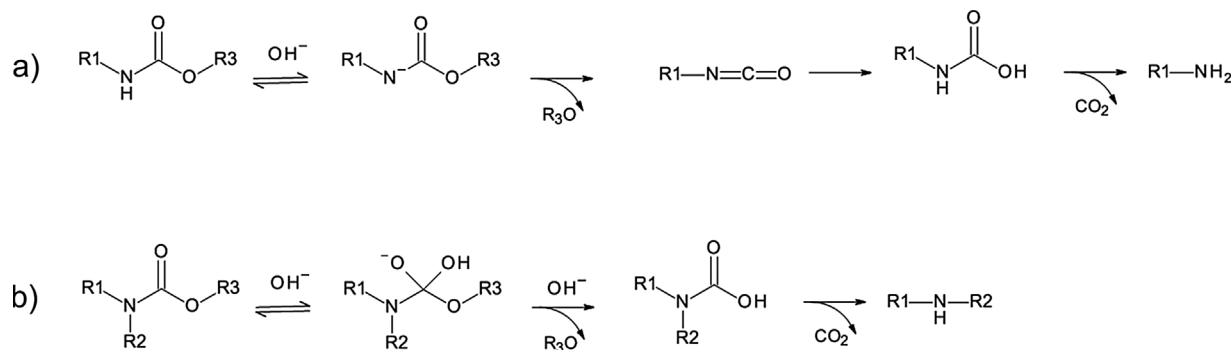


Fig. 1. Carbamate hydrolysis mechanisms, including a) E1cb (primary carbamates) and b) B<sub>AC</sub>2 (secondary carbamates).

tracers for the specific boundary conditions in various reservoirs.

## 2. Theoretical background

### 2.1. Reaction mechanism

Depending on the molecular structure of the carbamate, the hydrolysis reactions may proceed via two mechanisms: the elimination reaction (E1cb) or the acyl-oxygen bond cleavage (B<sub>AC</sub>2) (Drossman et al., 1988; Hegarty and Frost, 1973). Primary carbamates ( $R_1$  = alkyl/aryl,  $R_2$  = H, Fig. 1a) follow the E1cb mechanism in which the N–H group is deprotonated, resulting in the subsequent formation of isocyanate. This isocyanate intermediate is quickly hydrolyzed to form the carboxylated amine, which loses carbon dioxide spontaneously to yield the free amine.

An alternative mechanism (B<sub>AC</sub>2) is available to secondary carbamates ( $R_1, R_2$  = alkyl/aryl, Fig. 1b) in which a tetrahedral intermediate is formed by the nucleophilic attack of a hydroxide anion on the carbonyl carbon. The alkoxide ( $R_3O^-$ ) is subsequently expelled to produce the carboxylated amine, which then decomposes to carbon dioxide and the amines. An alcohol/phenol, carbon dioxide, and amine are formed as reaction products in the reaction shown in Fig. 1.

### 2.2. Reaction kinetics and thermo-sensitivity

The hydrolysis of a carbamate can proceed via three distinct bimolecular mechanisms, including acid, neutral, and base catalyzed.

$$\text{Acid catalyzed rate} = -k_A \cdot [H^+][\text{Carbamate}] \quad (1)$$

$$\text{Neutral catalyzed rate} = -k_{H_2O} \cdot [H_2O][\text{Carbamate}] \quad (2)$$

$$\text{Base catalyzed rate} = -k_B \cdot [OH^-][\text{Carbamate}] \quad (3)$$

where  $k_A$ ,  $k_{H_2O}$ , and  $k_B$  are second order rate constants;  $[H^+]$ ,  $[H_2O]$ , and  $[OH^-]$  are the concentrations of the catalysts; and  $[\text{Carbamate}]$  is the concentration of the reactant (thermo-sensitive tracer).

The overall hydrolysis rate is equal to the sum of all individual mechanisms. Hence, the combined rate constant  $k_h$  is defined by:

$$k_h = k_A \cdot [H^+] + k_{H_2O} \cdot [H_2O] + k_B \cdot [OH^-] \quad (4)$$

According to Larson and Weber (1994), the base catalyzed hydrolysis of carbamates tends to be more dominant in common natural systems than acid catalyzed and neutral catalyzed hydrolysis. As a result,  $k_h$  simplifies to:

$$k_h = k_B \cdot [OH^-] \quad (5)$$

Consequently, the kinetics of carbamate hydrolysis at constant pH/pOH exhibits pseudo-first-order kinetics similar to those of amides (Schaffer et al., 2016) and is expressed by:

$$-\frac{d[\text{Carbamate}]}{dt} = -k_h \cdot [\text{Carbamate}] \quad (6)$$

The kinetics of carbamate hydrolysis may also be determined by monitoring the concentration of the reaction product  $[\text{Amine}]$ :

$$\frac{d[\text{Amine}]}{dt} = k_h \cdot [\text{Amine}] \quad (7)$$

The temperature dependence of the reaction rate constant  $k_h$  is an essential factor for estimating the thermo-sensitivity of carbamate hydrolysis, and it follows Arrhenius' law:

$$T = -\ln \frac{A}{k_h} \cdot \frac{E_a}{R} \quad (8)$$

where  $A$  is the pre-exponential factor,  $E_a$  represents the activation energy for the reaction,  $R$  is the ideal gas constant, and  $T$  is the equivalent temperature of the reservoir. Therefore, by knowing the Arrhenius parameters  $E_a$  and  $A$ ,  $k_h$  can be determined for various  $T$  values and vice versa. This is important for the determination of the degree of cooling of the reservoir (Maier et al., 2015a,b).

## 3. Materials and methods

### 3.1. Carbamates and other chemicals

Eight structurally different primary carbamates were synthesized based on the acylation of primary amines (Idzik et al., 2015). These carbamates are highly soluble, and thus a non-sorbing behavior is probable due to the anionic sulfonic group attached to the molecules (Schaffer and Licha, 2014). One secondary carbamate (dimethyl-carbamic acid phenyl ester, 98%) was purchased from abcr GmbH. The carbamates investigated (C1–C9) in this systematic laboratory study, in which the focus lies on the relationship between the molecular structure and the hydrolysis speed, are deliberately designed based on stability and detectability. For the latter, the carbamates do not show fluorescence while one product (H1–H3) does to ease investigation efforts (Table 1).

The corresponding hydrolysis products 4-aminobenzenesulfonic acid (H1) from carbamates C1–C4 and 4-amino-3-methyl-benzenesulfonic acid (H2) from carbamates C5–C8 were obtained from Sigma-Aldrich, while phenol (H3) from carbamate C9 was provided by Merck. The phosphate salts (di-sodium hydrogen phosphate dihydrate and potassium dihydrogen phosphate) with analytical reagent grade employed for preparing the buffer solutions were purchased from Fisher Scientific. Ultrapure water used in all experiments was obtained from a combined water purification system consisting of Elix 5 and Milli-Q Gradient A10 (both from Merck Millipore). Individual stock solutions of the carbamates with  $c = 1 \text{ g L}^{-1}$  were prepared in dry dimethyl sulfoxide (DMSO) from AppliChem and stored in glass vials at 4 °C.

### 3.2. Evaluation of hydrolysis reaction kinetics

To investigate the hydrolysis reaction kinetics, the methods of Guggenheim and initial rates were applied. The selection of each

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