



# Application of the reaction class transition state theory to the kinetics of hydrogen abstraction reactions of alkanes by atomic chlorine

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## ABSTRACT

Kinetics of the hydrogen abstraction reaction of the class alkane + Cl → alkyl + HCl was studied using reaction class transition state theory (RC-TST) combined with linear energy relationships (LERs). The thermal rate coefficients for the reference reaction of ethane + Cl → ethyl + HCl, calculated by the micro-canonical variational transition state theory (μVT) incorporating small curvature tunneling (SCT), were taken from the literature. All necessary parameters were derived from density functional theory (DFT) calculations for a representative set of 29 reactions involving a range of hydrocarbons. Direct comparison to available experimental data reveals that the RC-TST/LER can predict rate coefficients for any reaction in the reaction class with acceptable accuracy. For the two test reactions outside of the representative set, our derived rate coefficients were in reasonable agreement with available data. Furthermore, our analyses indicate that RC-TST/LER gave systematic errors of less than 25% when compared to TST with one-dimensional Eckart tunneling approximation rate coefficients.

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## 1. Introduction

Hydrogen abstraction reactions involving alkanes and atomic chlorine (Cl) are a significant class of reactions in atmospheric chemistry and combustion chemistry. More than 60 theoretical and experimental studies for the reaction  $\text{CH}_4 + \text{Cl} \rightarrow \text{HCl} + \text{CH}_3$  have been published and about 40 theoretical and experimental studies have appeared for the reaction  $\text{C}_2\text{H}_6 + \text{Cl} \rightarrow \text{HCl} + \text{C}_2\text{H}_5$  [1]. The fate of Cl is not well-characterized since the rate coefficients for its reactions with many hydrocarbons, including alkanes, are not completely understood. These reactions are the major removal process for alkanes and other hydrocarbons in the global troposphere and marine boundary layer [2]. Despite their importance, there are only 13 such elementary reactions of alkane + Cl for which some direct experimental measurements of kinetic data are available, and these are available only over limited temperature ranges. Of these 13 reactions, only three reactions have been studied more than twice, and for four reactions, rate coefficients only at room temperature are reported. Experimental difficulties include secondary reactions of the intermediate alkyl radicals and instrumental limitations for wide temperature ranges. To construct the global detailed kinetic mechanisms for all possible reactions, rate

coefficients of all of the reactions in the class are needed. Recently, first-principles based theoretical calculations are providing an alternative route to the necessary kinetic information for hydrogen abstractions by Cl [3–5].

Rate coefficients for a large number of reactions in a given class can be estimated using the reaction class transition state theory with linear energy relationship (RC-TST/LER) method. The RC-TST/LER theory provides a cost-effective approach to estimating the thermal rate coefficients of all arbitrary reactions in the given class under the transition state theory framework. The central principle of RC-TST is that all reactions in the same class have the same reactive moiety involved in bond changes during the reaction, and thus are expected to have similar features on their potential surfaces along the specific reaction pathway. Rate coefficients of any reaction in the given class can be determined by the extrapolation from that of a reference reaction with a relative rate scaling factor expression that applies to the whole class. Moreover, within a given reaction class there is a linear energy relationship (LER) between the classical barrier heights and reaction energies [6–8]. By combining the basics of RC-TST with LER, thermal rate coefficients for any reaction in the class can be predicted from just its reaction energy once all reaction class parameters are determined. The definitions of these parameters are given in Section 2.1. Within the RC-TST/LER method the reaction energy can be simply obtained at a relatively low level of theory, e.g., AM1. Although AM1 is a low level of theory, it has proven to be very practical when combined with RC-TST/LER. Thus the use

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of AM1 makes RC-TST/LER a cost effective method for predicting thermal rate coefficients. Successful applications of RC-TST/LER have been demonstrated by a large number of studies in various systems [6,9–11].

The purpose of this study is to provide first-principles based kinetics information for hydrogen abstraction from various alkanes by Cl. The aim is to determine reaction class parameters for the alkane + Cl system. To do so, a representative set of hydrogen abstractions by Cl from alkanes at different positions in this class was selected and then explicit rate calculations by TST were performed. Finally, all reaction class parameters were determined by deriving correlated factors for the rate coefficients of reactions in the representative set of the class relative to the chosen reference reaction, for which highly accurate rate coefficients are derived from either experiment or theoretical calculation. To determine RC-TST/LER parameters for alkane + Cl class, 29 reactions involving 13 different alkanes are considered as a representative set. These reactions are shown below:

alkane + Cl	→ HCl + alkyl	
$C_2H_6 + Cl$	→ HCl + $\underline{C}H_3CH_3$	(R01) <i>p</i>
$C_3H_8 + Cl$	→ HCl + $\underline{C}H_3CH_2CH_3$	(R02) <i>p</i>
	→ HCl + $\underline{C}H_3CHCH_3$	(R03) <i>s</i>
$n-C_4H_{10} + Cl$	→ HCl + $\underline{C}H_3(CH_2)_2CH_3$	(R04) <i>p</i>
	→ HCl + $\underline{C}H_3CH_2CHCH_3$	(R05) <i>s</i>
$iso-C_4H_{10} + Cl$	→ HCl + $\underline{C}H_3CH(CH_3)CH_3$	(R06) <i>p</i>
	→ HCl + $\underline{C}H_3C(CH_3)CH_3$	(R07) <i>t</i>
$n-C_5H_{12} + Cl$	→ HCl + $\underline{C}H_3(CH_2)_3CH_3$	(R08) <i>p</i>
	→ HCl + $\underline{C}H_3(CH_2)_2CHCH_3$	(R09) <i>s</i>
	→ HCl + $\underline{C}H_3CH_2CHCH_2CH_3$	(R10) <i>s</i>
$iso-C_5H_{12} + Cl$	→ HCl + $\underline{C}H_3CH(CH_3)CH_2CH_3$	(R11) <i>p</i>
	→ HCl + $\underline{C}H_3CH(CH_3)CH_2CH_2$	(R12) <i>p</i>
	→ HCl + $\underline{C}H_3CH(CH_3)CHCH_3$	(R13) <i>s</i>
	→ HCl + $\underline{C}H_3C(CH_3)CH_2CH_3$	(R14) <i>t</i>
$neo-C_5H_{12} + Cl$	→ HCl + $\underline{C}H_3C(CH_3)_2CH_3$	(R15) <i>p</i>
$n-C_6H_{14} + Cl$	→ HCl + $\underline{C}H_3(CH_2)_4CH_3$	(R16) <i>p</i>
	→ HCl + $\underline{C}H_3(CH_2)_3CHCH_3$	(R17) <i>s</i>
	→ HCl + $\underline{C}H_3(CH_2)_2CHCH_2CH_3$	(R18) <i>s</i>
$iso-C_6H_{14} + Cl$	→ HCl + $\underline{C}H_3CH(CH_3)(CH_2)_2CH_3$	(R19) <i>p</i>
	→ HCl + $\underline{C}H_3CH(CH_3)(CH_2)CH_2$	(R20) <i>p</i>
	→ HCl + $\underline{C}H_3CH(CH_3)CH_2CHCH_3$	(R21) <i>s</i>
	→ HCl + $\underline{C}H_3CH(CH_3)CHCH_2CH_3$	(R22) <i>s</i>
$CH_3CH_2CH(CH_3)CH_2CH_3 + Cl$	→ HCl + $\underline{C}H_3CH_2CH(CH_3)CH_2CH_2$	(R23) <i>p</i>
	→ HCl + $\underline{C}H_3CH_2CH(CH_3)CHCH_3$	(R24) <i>s</i>
	→ HCl + $\underline{C}H_3CH_2CH(CH_2)CH_2CH_3$	(R25) <i>p</i>
$CH_3CH(CH_3)CH(CH_3)CH_3 + Cl$	→ HCl + $\underline{C}H_3CH(CH_3)CH(CH_2)CH_3$	(R26) <i>p</i>
$neo-C_6H_{14} + Cl$	→ HCl + $\underline{C}H_3C(CH_3)_2CH_2CH_3$	(R27) <i>p</i>
	→ HCl + $\underline{C}H_3C(CH_3)_2CH_2CH_2$	(R28) <i>s</i>
	→ HCl + $\underline{C}H_3C(CH_3)_2CHCH_3$	(R29) <i>p</i>

where the underlined carbon atom,  $\underline{C}$ , contains the radical site in the products of hydrogen abstraction reactions. Of these 29 reactions, 16 reactions represent hydrogen abstractions from the primary carbons (*p*), 11 reactions represent hydrogen abstractions from the secondary carbons (*s*) and two reactions represent hydrogen abstractions from the tertiary carbons (*t*).

## 2. Methodology and computational details

### 2.1. Reaction class transition state theory (RC-TST)

Since details of the RC-TST/LER method has been given in detail in previous reports [6,7], we focus on the necessary parameters here. Within the RC-TST framework, the rate coefficient of an arbitrary reaction (denoted as  $R_a$ ) in a given reaction class,  $k_a(T)$ , is proportional to the rate coefficient of the reference reaction (denoted as  $R_r$ ) of the class,  $k_r(T)$ . The proportionality function,  $f(T)$  is a temperature-dependent relative rate function.

$$k_a(T) = f(T)k_r(T) \quad (1)$$

For the reference reaction, one generally selects the smallest reaction (having the least number of atoms) in which it can represent the behaviors of chemical moiety for the whole class.

Moreover, rate coefficients of the smallest reaction can be calculated accurately from first principles using high level of theory. The key approach of the RC-TST method is to factor  $f(T)$  into different components:

$$f(T) = f_{\kappa}(T)f_{\sigma}f_Q(T)f_V(T)f_{HR}(T) \quad (2)$$

where  $f_{\kappa}$ ,  $f_{\sigma}$ ,  $f_Q$ ,  $f_V$  and  $f_{HR}$  are tunneling, symmetry number, partition function, potential energy and hindered rotor factors, respectively. These factors are simply the ratio of the corresponding components in the well-known TST expression for the two reactions:

$$f_{\kappa}(T) = \frac{\kappa_a(T)}{\kappa_r(T)} \quad (3)$$

$$f_{\sigma} = \frac{\sigma_a}{\sigma_r} \quad (4)$$

$$f_Q(T) = \left( \frac{Q_a^{\ddagger}(T)}{\Phi_a^R(T)} \right) / \left( \frac{Q_r^{\ddagger}(T)}{\Phi_r^R(T)} \right) = \left( \frac{Q_a^{\ddagger}(T)}{Q_r^{\ddagger}(T)} \right) / \left( \frac{\Phi_a^R(T)}{\Phi_r^R(T)} \right) \quad (5)$$

$$f_V(T) = \exp \left[ -\frac{(\Delta V_a^{\ddagger} - \Delta V_r^{\ddagger})}{k_B T} \right] = \exp \left[ -\frac{\Delta \Delta V^{\ddagger}}{k_B T} \right] \quad (6)$$

$$f_{HR}(T) = \frac{HR_a(T)}{HR_r(T)} \quad (7)$$

where  $\kappa(T)$  is the transmission coefficient accounting for the quantum mechanical tunneling effects,  $\sigma$  is the reaction symmetry number,  $Q^{\ddagger}$  and  $\Phi^R$  are the total partition functions (per unit volume) of the transition state and reactants, respectively,  $\Delta V^{\ddagger}$  is the classical barrier height,  $HR$  symbolized the total partition function due to the hindered rotor approximation,  $T$  is the temperature in Kelvin, and  $k_B$  is the Boltzmann constant.

The important task is to derive general expressions for these factors linking the rate coefficients of  $R_r$  and those of  $R_a$  in the same class without having to calculate  $k_a(T)$  explicitly. This is done by performing explicit rate determinations for the above representative set of reactions using the TST with the one-dimensional Eckart tunneling approximation [12,13] (TST/Eckart) then analyzing the 'exact' calculated relative rate factors as functions of temperature to derive general expressions for the whole class. The rationale for using the TST/Eckart method for this purpose has been discussed previously [6,7,9]. The calculated barrier heights and reaction energies for the above representative set of reactions also allow us to determine the LER between them that also can be used for the entire class.

Comparisons of rate coefficients derived from our RC-TST/LER parameters with available experimental data from the literatures and from our explicit TST/Eckart for R01–R29 reactions are presented. In addition, our RC-TST/LER parameters are further applied to estimate thermal rate coefficients for two test cases outside of the representative set. Validation of these two test cases will be analyzed and discussed.

### 2.2. Electronic structure calculations

All the electronic structure calculations were performed using the Gaussian 03 suite of program [14]. The geometries and harmonic vibrational frequencies of all the stationary points for all reactions in the given class (the reactants, transition state, and products) were calculated at the hybrid BH&HLYP level of density functional theory with the cc-pVDZ basis set. The BH&HLYP method was found previously to be sufficiently accurate for predicting the transition state properties for hydrogen abstraction reactions by a radical [15–17]. For the reference reaction, rate coefficients calculated at the micro-canonical variational transition state theory ( $\mu$ VT) augmented with

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