THEORETICAL DETERMINATIONS OF REACTION PARAMETERS
FOR ATMOSPHERIC CHEMICAL REACTIONS

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Abstract. The most common methods for estimating rate constants for elementary
and complex atmospheric chemical reactions are presented. The presented methods
are categorized into dynamical, statistical-dynamical and statistical methods. The type
of information about the system that is needed in order to estimate the rate constant is
discussed. The bottleneck in these methods is the accuracy of the potential energy
surface/reaction path. This problem is discussed and recommendations of methods are
given.

Keywords: Atmospheric chemical reaction, theoretical estimation of rate constant, potential
energy information, Electronic Structure Theory (ab initio, Density Functional Theory), Variation
Transition State Theory

1. Introduction

Mechanisms of atmospheric chemical reactions are used to predict the effects of
emissions on the atmospheric chemical composition from the atmospheric boundary
layer to the top of the stratosphere. These mechanisms should include all the
important chemical reactions with their rate constants in order to make accurate
predictions of the chemical composition of interest. Unfortunately this is not an easy
task because the organic chemistry of the polluted atmosphere is extremely
complicated (Atkinson et al., 2004, 2006, 2007; Sander et al., 2006; Gery et al., 1989;
Andersson-Sköld and Simpson, 1997, Simpson et al., 1997, Stockwell et al., 1997;
Carter, 2000).

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An important weakness of detailed gas-phase chemical mechanisms is that relatively few rate constants have been measured. Many of the rate parameters and product yields for organic compounds that are emitted into the atmosphere are difficult to measure because many of these reactions have multiple channels with relatively low product yields (Seinfeld and Pandis, 1997; Finlayson-Pitts, 2000). Most of the rate parameters and product yields used in highly detailed mechanisms of atmospheric chemical reaction are estimated from analogy with known reactions or through empirical structure-reactivity relationships. The uncertainty in these estimated rate parameters is usually greater for the more reactive organic compounds. Even for those reactions with measured rate parameters, the temperature dependence is not well characterized (Atkinson et al., 2004, 2006, 2007; Sander et al., 2006). The temperature dependence of the rate constants is important because the ambient temperature of the troposphere spans a range from near 300 K in the lower troposphere down to about 200 K near the tropopause (Warneck, 1988). Due to experimental limitation rate parameters are most accurately known around 298 K (Atkinson et al., 2004, 2006, 2007; Sander et al., 2006).

Methods often used to calculate rate constant for unknown reactions are structural correlation methods (Kirchner and Stockwell, 1996; Madronich and Calvert, 1990; Wayne et al., 1991). The disadvantage of these methods is that they may have errors on the order of $10^7$ to $10^9$.

Due to the reasons listed above theoretical calculations, which enable the estimation of rate parameters, have the possibility of improving mechanisms of atmospheric chemical reactions. If a computational method could at least provide the relative magnitude of rate parameters for the reactions, the method could be used to determine branching ratios and trends. Such information would be of interest for the further development of the chemical mechanisms.

The goal of this paper is to describe the most commonly used methods to calculate elementary chemical rate constants when no exterior forces (e.g. electric or magnetic fields) are acting on the system. We emphasize the problems related to the use of the various methods. We address the type of information about a given system that is needed in order to estimate a rate constant. Above we stressed that it is difficult to experimentally measure rate constants at temperatures very different from 298 K. In contrast theoretical models can estimate temperature dependence if sufficient information about the system of interest is available.

In all of the theoretical methods described in this paper (Section 2), Potential Energy Information (PEI) (i.e. ab initio and Density Functional Theory (DFT) calculations) of high quality are of fundamental importance (Section 3). The applicability of the methods is discussed in Section 4; the discussion is based on practical examples.