



Atmospheric reaction of chlorine radical and cyclic amide: A theoretical approach

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ABSTRACT

The atmosphere is considered a chemical reactor where many chemical reactions occur. Theoretical investigations are useful for understanding the mechanisms involved in the reaction with atmospheric radicals. Density functional theory (DFT) with B3LYP, CBS-QB3 and G3B3 methods were used to investigate the reactivity, mechanism and structure–reactivity relationship as well as the kinetics of *N*-methyl-2-pyrrolidinone (NMP) reaction with chlorine. Furthermore, the Rice–Ramsperger–Kassel–Marcus (RRKM) theory was employed to compute the rate constants. This study provides rate coefficients and a detailed H-abstraction mechanism for the reaction of chlorine with NMP. Kinetic and mechanistic results showed that the mechanism of this reaction goes with small barriers through H-atom transfer from the $-\text{N}-\text{CH}_3$ group and $-\text{CH}_2-$ adjacent to the $-\text{N}-\text{CH}_3$ site within a branching ratio slightly in favour of the $-\text{N}-\text{CH}_3$ site.

1. Introduction

The study of the chlorine reaction with volatile organic compounds (VOCs) is important for atmospheric observations regarding tropospheric pollution. It has provided models for investigating the dynamics and kinetics of reactions in the gas phase. VOCs constitute a major class of chemicals emitted directly into the troposphere. H-abstraction from these compounds provides an important source of O_3 and other photochemical pollutants in coastal and industrialized areas [1]. Amides form a wide variety of nitrogen-containing volatile organic compounds (NVOCs), which are considered to be primary or secondary pollutants [2]. The reaction of amides with atmospheric radicals shows the involvement of these contaminants into the tropospheric lifetime in relation to each atmospheric photo-oxidant [1–5]. The reactions of amides were carried out under atmospheric conditions. Koch *et al.* [6] used flash/fluorescence resonance photolysis to study the oxidation kinetics of amides using OH radicals at various temperatures, whereas Aschmann and Atkinson [7] performed the relative rate technique to study the OH and NO_3 homogeneous oxidation kinetics of *N*-methyl-2-pyrrolidinone (NMP). Furthermore, the reaction kinetics of amides with OH and Cl radicals at room temperature were determined [8]. On the other hand, the radical reaction of NO_3 with certain amides at different

temperatures was investigated and the rate coefficient using laser photolysis coupled with UV–visible spectroscopy as well as time-resolved absorption was determined [9]. In the absence of experimental mechanistic investigations through isotope labelling, the kinetic results seem to indicate that the reactions of amides with atmospheric oxidants are sensitive to the amide structure.

Consequently, mechanistic and theoretical studies are useful for understanding the mechanisms involved in the reaction with atmospheric radicals. The B3LYP method [10] overestimates H-abstraction barriers and provides unreliable thermochemical values. In fact, current studies showed that the CBS-QB3 method [11] frequently gives good agreement with experimental reaction energies and barriers for molecules having the same size as those involved in this work [12–14]. Furthermore, G3B3 [15] is useful for larger open-shell systems with a very low spin contamination (~ 1 kcal/mol for the neutral set of molecule) [12,15].

Having low volatility, high chemical and thermal stability, NMP is considered a replacement for some organic solvents [6]. In fact, little information is available on the mechanisms of amide degradation by atmospheric oxidants. This research reports hence a theoretical investigation of the kinetics and structure–reactivity mechanism of the reaction taking place between a chlorine atom with a cyclic amide,

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