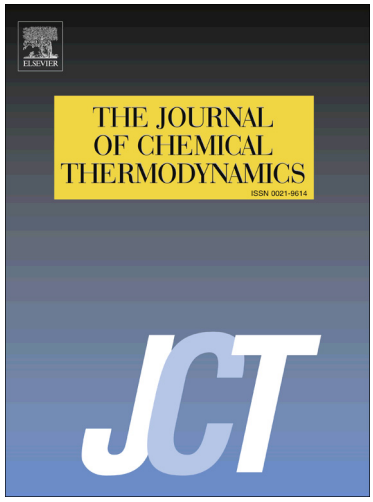

Computational study of the hydrolysis of carbonyl sulphide: thermodinamics and kinetic constants estimation using *ab-initio* calculations

Á. Vidal-Vidal, M. Pérez-Rodríguez, M.M. Piñeiro

PII: S0021-9614(17)30063-0
DOI: http://dx.doi.org/10.1016/j.jct.2017.03.003
Reference: YJCHT 4997

To appear in: *J. Chem. Thermodynamics*

Received Date: 22 November 2016
Revised Date: 16 February 2017
Accepted Date: 1 March 2017

Please cite this article as: Aacute. Vidal-Vidal, M. Pérez-Rodríguez, M.M. Piñeiro, Computational study of the hydrolysis of carbonyl sulphide: thermodinamics and kinetic constants estimation using *ab-initio* calculations, *J. Chem. Thermodynamics* (2017), doi: http://dx.doi.org/10.1016/j.jct.2017.03.003

Computational study of the hydrolysis of carbonyl sulphide: thermodinamics and kinetic constants estimation using *ab-initio* calculations.

Á. Vidal-Vidal, M. Pérez-Rodríguez, and M.M. Piñeiro*

* *Departamento de Física Aplicada, Universidade de Vigo, Spain; E-mail: mmpineiro@uvigo.es*

Abstract

Carbonyl sulphide is the predominant sulphur compound in the atmosphere, contributing to the formation of aerosol particles affecting global climate. Human activity has significantly increased its total amount since the beginning of the Industrial Revolution due to its presence in petroleum and coal, reason why it is necessary to understand and control its emissions. On the other hand, carbonyl sulphide is an undesired substance for catalysis in important industrial processes. Hydrolysis is the most promising among the different strategies to reduce its presence, giving as products carbon dioxide and hydrogen sulphide. In the present work, the mechanism of reaction of carbonyl sulphide hydrolysis process in gas phase was studied from 400 K to 1500 K, equilibrium constants were obtained and reaction yields were estimated, by means of composite quantum-computational methods. Good agreement with literature experimental results confirms the suitability of the chosen methods, specially CBS-QB3, in supporting the reaction mechanism, giving accurate equilibrium constant values, and obtaining realistic yields. The effect of isotopic substitution in OCS was also studied, from 300 K to 1500 K, being much less significant than temperature dependence.

Keywords: Hydrolysis, Carbonyl sulphide, Composite methods, DFT, Computational study

1. Introduction

Since the discovery of the presence of carbonyl sulphide (OCS) in tropospheric air, it has been recognized as the predominant sulphur-bearing atmospheric compound[1, 2, 3]. The mixing ratio of OCS has increased significantly from an initial value around 372 parts-per-trillion in volume (pptv) before industrial revolution[4], to reach approximately 500 pptv nowadays[5, 6, 7]. It can be produced either naturally, as a result of volcanic activity or forest fires, or by anthropogenic sources, as the process of coal gasification and fuel combustion. It is important to control its emission rate and overall atmospheric amount due to the contribution to the formation of stratospheric aerosol particles [8], that affect the Earth's climate[9] due to the modification of radiation balance. It is worth pointing out that the tropospheric lifetime of OCS [10] is quite long (1-6 years [3, 11]), while, when it eventually reaches the stratosphere[8], its lifetime increases until 64 ± 21 years [12].

Since OCS and CS_2 are the major organic sulphur compounds in petroleum, crude oil and coal compositions, and it is extremely harmful for catalysts used in several industrial processes (such as fluid catalytic cracking or the Fischer-Tropsch process), several methods have been developed so far for their capture. For example, in the Fischer-Tropsch process, besides that the product selectivity is affected by sulphur poisoning, the presence of only 4mg of sulphur per gram of Fe-Cu-K catalyst reduces activity by a 50 % [13], and therefore, raw materials must undergo desulphuration processes. Among all methods, the main applied technologies can be classified as: adsorption and absorption (Eqs. 1 and 2) [14, 15, 16, 17, 18, 19], hydrogenation (Eq. 3) [20], oxidation (Eqs. 4 and 5) [21, 22], , photolysis (Eq. 6) [23], and hydrolysis (Eq. 7) [24, 25, 26]. The latter can be either catalytic or non-catalytic.

Among these methods, hydrolysis has been recognized as the most promising process due to its high conversion efficiency and mild reaction conditions.

Over the years, hydrolysis mechanisms of linear molecules such as CO_2 have been studied employing either experimental[27] or a wide variety of computational methods [28, 29, 30]. The most recent works have applied successfully sophisticated computational methods, due to the high advances on the development of computational resources. For example, in the case of CO_2, Nguyen *et al.* [31] studied the hydrolysis at QCISD(T) and MP2 levels, in both vacuum and water (simulated with continuum models such as SCRF and PCM), in order to determine the number of water molecules that are actively involved on the neutral hydration of CO_2 to form H_2CO_3. Other authors explored the possibility of having more than one water molecule acting catalytically due to the alleviation of ring strain in proton-transfer transition state. Lewis *et al.*[32] computed activation barriers up to three water molecules with different MPn methods. CO_2 is not the only molecule studied, as other analogs and cumules having a general structure X=C=X with X=O,S, NH, among others: CS_2, H_2C=O, and even HN=C=NH, have been also object of research [33, 34, 35, 36, 37, 38, 39, 40]. OCS may as well form clathrate hydrates [41], and calculation schemes similar to the ones tested here have proved to be quantitative in the description of thermodynamics and structure of this type of