

Relative rate and product studies of the dimethyl ether and diethyl ether reactions with chlorine atoms

Diogo J. Medeiros,^{1,*} Iustinian Bejan,² and Paul W. Seakins^{1,3}

¹ School of Chemistry, University of Leeds. Leeds. UK

² Integrated Center for Studies in Environmental Science for Northeast Region Romania (CERNESIM), University of Iasi, Iasi, RO.

³ National Centre for Atmospheric Science, University of Leeds, Leeds, UK

* Corresponding author: cmdj@leeds.ac.uk

Ethers are important oxygenated organic compounds widely used as industrial solvents and fuel additives. Once released into the atmosphere, their oxidation is primarily initiated by the reaction with the hydroxyl radical (OH). The oxidation of volatile organic compounds (VOCs) initiated by their reaction with chlorine atoms (Cl) is an important atmospheric removal process, especially in the marine boundary layer (MBL). The averaged concentration of Cl atoms in the MBL of the North Atlantic can increase from $3.3 \times 10^4 \text{ Cl cm}^{-3}$ at dawn to $6.5 \times 10^4 \text{ Cl cm}^{-3}$ at noontime⁽¹⁾ while the concentration above the Antarctic Ocean was estimated around 720 Cl cm^{-3} .⁽²⁾ Ethers have a relatively short lifetime in the atmosphere and hence is unlikely that their transportation to regions where Cl chemistry can dominate will occur significantly, however, there is evidence that Cl precursors are also abundant in continental regions.⁽³⁾

Within this work the reactions of dimethyl ether (DME) and diethyl ether (DEE) with Cl atoms were investigated. A combination of kinetic assessments and product studies of these reactions were performed using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)⁽⁴⁾, a temperature controlled cylindrical reaction vessel made of grade 304 stainless steel and equipped with a wide variety of instruments (FTIR, HOx radicals detection, gas chromatography, etc.) which allow both reagents and products concentrations to be monitored over time. According to our preliminary results the first-generation yield of methyl formate from the Cl + DME reaction is $0.97 \pm (0.06)$ for a free linear fit and $0.88 \pm (0.04)$ forcing a fit through the origin, in good agreement with the yield reported by Japar et al.⁽⁵⁾ The measured rate coefficient for the diethyl ether + Cl reaction is $k = (3.56 \pm 0.33) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Further experiments will be carried and their results will be properly addressed.

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References

- [1] OW Wingenter, MK Kubo, NJ Blake, TW Smith, DR Blake and FS Rowland, *J. Geophys. Res.-Atmos.*, **101** (1996) 4331-4340.
- [2] OW Wingenter, DR Blake, NJ Blake, BC Sive, FS Rowland, E Atlas and F Flocke, *J. Geophys. Res.-Atmos.*, **104** (1999) 21819-21828.
- [3] JA Thornton, JP Kercher, TP Riedel, NL Wagner, J Cozic, JS Holloway, WP Dube, GM Wolfe, PK Quinn, AM Middlebrook, B Alexander and SS Brown, *Nature*, **464** (2010) 271-274.
- [4] DR Glowacki, A Goddard, K Hemavibool, TL Malkin, R Commane, F Anderson, WJ Bloss, DE Heard, T Ingham, MJ Pilling and PW Seakins, *Atmos. Chem. Phys.*, **7** (2007) 5371-5390.
- [5] SM Japar, TJ Wallington, JFO Richert and JC Ball, *Int. J. Chem. Kinet.*, **22** (1990) 1257-1269.