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

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1.Introduction

- Ethers are important oxygenated organic compounds widely used as industrial solvents and fuel additives.
- 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).
- 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.(1)
- Controlled experiments initiated by Cl are essential for aiding the elucidation of field measurements, providing valuable insights in both kinetic and mechanistic research. Simulation chambers represent suitable tools for this purpose.

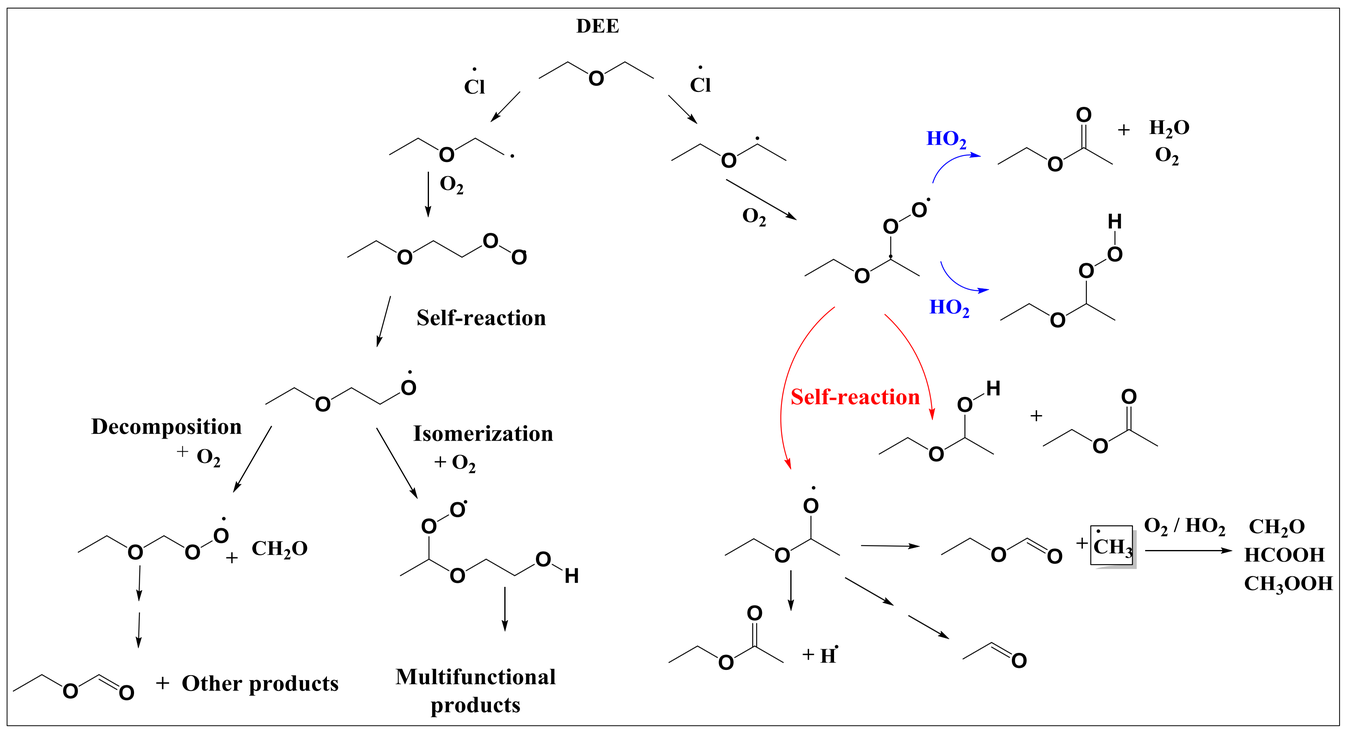

Figure 1. Chemical scheme for the diethyl ether oxidation upon reaction with chlorine atoms

2. Relative Rate Experiments

- All the experiments were performed in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) (2), a cylindrical reaction cell made of grade 304 stainless steel and equipped with a wide variety of instruments (Fourier transform infrared spectroscopy, HO_x radicals detection, gas chromatography, temperature control, etc.) .
- The experiments were performed in air, at 298 K and in the absence of NO.
- The typical concentration of Cl_2 in or experiments was ~5x10^{13} molecules cm^{-3}.

Ketone	Structure	Reference Compound	k_1/k_2	k_1 / 10^{-10} cm^3 molecule^{-1} s^{-1}	Literature k_1 / 10^{-10} cm^3 molecule^{-1} s^{-1}
Dimethyl Ether	$H_3C-O-CH_3$	i-butane	1.27±0.17	1.78±0.36	1.76±0.16[3]
Diethyl Ether	$H_3C-O-CH_3$	i-pentane	1.81±0.17	3.56±0.34	2.54±0.43[4] 2.57±0.43[4] 3.55±0.28[4]

Table 1. The relative ratios and the calculated rate constants for each investigated ether. The implemented values for the reference reactions were obtained from Atkinson et al. 2006 (5) for iisobutane and Hooshiyar et al. 1995. (6)

3. Product Studies

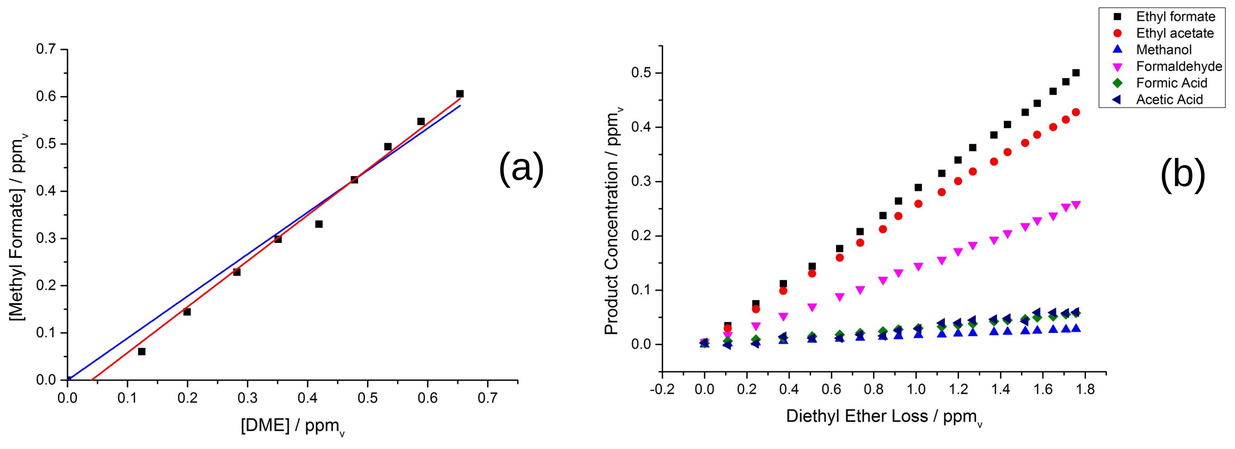

Figure 2. Yields of the identified products from the reactions of chlorine atoms with (a)dimethyl ether and (b) diethyl ether.

- These experiments were carried out under the same conditions presented for the relative rate studies.

DME + Cl

- Product studies of the dimethyl ether+ Cl reaction generated a first-generation yield of 0.97±0.03 for methyl formate.
- Minor formation of CH_3OCH_2OOH is observed.

DEE + Cl

- On a molar basis, the detected products for the diethyl ether + Cl reaction sums to ~75%. Orlando reported typical values between 70 and 90% at 298 K. (7)

Product	Ethyl Formate	Ethyl acetate	Formaldehyde	Acetic Acid	Formic Acid	Methanol
First generation Yield	0.28	0.24	0.14	0.037	0.031	0.016

Table 2. First generation yields for the detected products.

4. Conclusions and Future work

- The relative rate experiments performed in HIRAC allowed the calculation of the rate constant of the reactions of diethyl and dimethyl ether with chlorine atoms.
- It was possible to identify and quantify the main products from these reactions using Fourier Transform infrared spectroscopy.
- The measured product yields are in agreement with the values reported by Orlando.
- Further experiments for the DME + Cl at higher temperatures will elucidate the CH_3OCH_2OOH formation.
- Additional experiments on the DEE + Cl reaction will allow a survey on the current oxidation mechanism.

5. Acknowledgements

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