Furans

- the potential atmospheric impact of a next-generation bio fuel

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Abstract

There has been a worldwide debate about “the climate change” over the past years, accompanied with the efforts in finding a more environmental friendly way to live. One area of research is to find replacements for the fossil fuels, which is the major energy source today. The aim of this project is to investigate the atmospheric properties of a new potential group of biofuels, i.e. the group of compounds called furans, and especially the two molecules 2-Methyltetrahydrofuran and 2,2-Dimethyltetrahydrofuran. The reason for this is that the environmental impact of a large scale use must be well known before any production can be considered. Therefore the reaction between these molecules and the atmospheric chlorine atoms will be investigated with respect to reaction speed and what products that will be formed.

The project is based on experimental work performed at the Copenhagen Centre for Atmospheric Research. A smog chamber which can be filled with a desired mixture of atmospheric gases, can be exposed to UV-light for a specific time and a detector can register the infrared light from a laser that goes through the gas mixture. This was used to test how the reactions proceeded between chlorine atoms and 2-Methyltetrahydrofuran and 2,2-Dimethyltetrahydrofuran respectively. The speed of the reaction, which is represented by a rate constant, was determined by analysing data and using the relative rate method. The products were studied by comparing infrared spectra from different molecules.

The results from the experiments were that the rate constants for the two compounds have the values $k_{2\text{-}MTHF+Cl} = 1.3 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$ and $k_{2,2\text{-}DMTHF+Cl} = 1 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$. The products that are known to be formed are hydrogen chloride, HCl, carbon dioxide, CO_2, carbon monoxide, CO, water, H_2O and formic acid, HCOOH.

This project resulted in the conclusion that the reaction with chlorine is fast and can be very important in some urban areas. This work has been one of the first of its kind, and even if it does not absolutely describe the atmospheric implications of these two potential fuels, it has laid a foundation for future research in the area.

Populärvetenskaplig sammanfattning

På grund av den världsomfattande diskussionen rörande ”klimatförändringen” som pågått under de senaste åren, så har försök gjorts för att få människor att ändra sina vanor och för att hitta alternativa energikällor. I dag är det fossila bränslen som dominerar som energikällor men eftersom de ger upphov till höga koldioxidhalter pågår det forskning för att ta fram alternativa bränslen. En grupp av ämnen som har föreslagits är de som kallas furaner, som kan framställas av socker och som brinner väldigt lätt. De två ämnen som undersöks är 2-Metyltetrahydrofuran och 2,2-Dimetyltetrahydrofuran. Det är viktigt att ta reda på hur dessa ämnen kommer reagera med andra ämnen som finns i atmosfären för att kunna undersöka hur de kommer påverka miljön. Målet med detta arbete är därför att undersöka hur dessa ämnen skulle reagera med kloratomer i atmosfären om de eventuellt skulle börja användas i större skala.

Experiment utfördes i ett laboratorium på Copenhagen Centre for Atmospheric Research. I en så kallad smog kammare kan en valfri blandning av gaser som liknar en sammasättning i atmosfären undersökas. Reaktionerna undersöks med avseende på hur mycket blandningen bestrålats av UV-ljus. Det som undersöktes var hur snabbt reaktionerna mellan 2-Metyltetrahydrofuran respektive 2,2-Dimetyltetrahydrofuran och klor sker, dvs. reaktionernas hastighetskonstant, samt vilka produkter som bildas.

Resultaten analyserades med hjälp av dataprogram och de produkter som bland annat bildas är väteklorid, HCl, koldioxid, CO_2, kolmonoxid, CO, vatten, H_2O och myrsyra, HCOOH. De värden på hastighetskonstanterna som erhölls var: $k_{2\text{-}MTHF+Cl} = 1.3 \cdot 10^{-10}$ $cm^3molekyl^{-1}s^{-1}$ och $k_{2,2\text{-}DMTHF+Cl} = 1 \cdot 10^{-10}$ $cm^3molekyl^{-1}s^{-1}$. Slutsatserna som kan dras av detta är att klor reagerar mycket snabbt med dessa ämnen och att det kan ha betydelse i områden där klorhalterna i luften är förhöjda, till exempel på grund av luftföroreningar.

Detta är första gången som dessa reaktioner mellan 2-Metyltetrahydrofuran respektive 2,2-Dimetyltetrahydrofuran och klor undersöks. Även om dessa potentiella biobränslens påverkan på atmosfären och miljön inte är fullt kartlagda än, så har idéerna och undersökningsmetoden förbättrats och kan förhoppningsvis vara till hjälp för framtida forskning inom området.

Table of contents

1. Background

The background of this work arises from the interests in the resulting climate effects of the new potential biofuel based on furan derivatives. The climate system and its sensitivity to changes is briefly explained and the chemical compounds called furans are presented with focus on their properties as a fuel and an atmospheric constituent. In the end some goals are set up for this work with a focus on atmospheric chemistry involving furans.

1.1 Climate and climate changes

1.1.1 The climate system and energy budget of the Earth

The condition on the Earth's surface and in the air that surrounds it, averaged over a long period of time, is what is typically called the climate [1], [2]. The everyday change of the conditions on a particular location is called weather. The long term variations for larger areas, during an average period of 30 years, of the same meteorological variables that determines the weather defines the climate. These properties are the surface temperature, especially, cloud cover, precipitation, surface pressure and chemical composition, e.g. oxygen concentration, etc.

The climate system is built up of the distribution of the surface types, land, ocean and ice, the atmosphere and the incoming radiation from the sun which provides the whole system with energy. The Earth has an energy budget, which means that it is in radiative balance so that the amount of energy that comes in is to a good approximation equal to the energy that is radiated back into space. Since the high clouds and ice covers reflect a lot of the incoming sunlight directly, about 30 %, these factors work as coolers for the Earth. Low clouds and a lot of the surface absorb the remaining 70 %. The light from the sun lies mainly in the visible wavelength region and is in this context called shortwave radiation. The Earth and the clouds emit radiation in the infrared wavelength region, called long wave radiation, due to the much lower surface temperature than the suns. Since the atmosphere is opaque to some wavelengths, e.g. UV light and some infrared regions, the outgoing radiation will be absorbed by the molecules in the atmosphere. This radiation is then reemitted in arbitrary directions, which gives the result that some radiation is reemitted back to the earth's surface. This is the definition of the well-known greenhouse effect, which if not present would result in an Earth with a mean surface temperature of about -17ºC instead of the present +18ºC [2]. It is however shown that the energy budget is not perfectly balanced, but there is a small net absorption of less than 1 W/m^2 out of the approximate 340 W/m^2 that reaches the top of the atmosphere from the sun [5].

1.1.2 The atmosphere

The atmosphere can roughly be divided into two main parts, the lower and the upper atmosphere. The part that is of main interest for climate and atmospheric chemistry is the lower part which is divided into the troposphere and the stratosphere. The troposphere extends from the Earth's surface up to the tropopause at about 10-20 km altitude [2], depending on the temperature of the air. The characteristic feature of the troposphere is a decreasing temperature with height and a large vertical mixing since the warmer air close to the surface can rise due to its lower density. The stratosphere extends from the tropopause up to about 50 km altitude and is characterized by an increasing temperature with height and thus a slow vertical mixing and stable air.

The exchange of air around the Earth occurs at different timescales. Some approximate magnitudes are 1-2 weeks around the earth on the same latitude, 1-2 months to reach the equator, 1 year to cross the equator, and 5-10 years to cross the tropopause. This is used in models that predict the circulation and spread of different atmospheric constituents like trace gases or aerosols. The slow exchange of air between the troposphere and the stratosphere gives largely different chemical conditions, e.g. the stratosphere is almost unaffected by the compounds that are emitted at the Earth's surface and have a shorter life time than approximately one year. The stratosphere is also more affected by the shortwave and UV radiation from the sun since almost all the UV light is absorbed before it reaches the Earth's surface. UV light is necessary for the formation of ozone and the stability and low mixing of the stratosphere gives rise to the ozone layer at approximately 25 km altitude.

1.1.3 Climate change

The climate is as mentioned in the previous sections dependent on a balance between many factors, and all of them can change with time. When a factor changes which can lead to changes in the climate it is called climate forcing [2]. Forcing is a measure of the possible influence that a factor has as a climate change mechanism. Most often it is a temperature change that is the result of a climate forcing. An example of an external climate forcing is the changes in the Earth's orbit around the sun which varies over large timescales of thousands of years and more. The distance to the sun and the solar activity are part of the radiative forcing, which refer to influence on the balance between the incoming short wave and the outgoing long wave radiation. An internal forcing can be the chemical composition of the atmosphere, including both gases and particles, e.g. the amount of greenhouse gases as carbon dioxide and methane.

A climate forcing does not necessary have to lead to a climate change, there can be many forcings acting at the same time leading to a cancellation effect. Since the climate system is complex and many factors are dependent of each other, a forcing may enhance or cancel out itself due to feedback [2]. An example of so called positive feedback, i.e. an enhanced change, is a small temperature decrease, leading to more ice forming on the Earth's surface, leading to a higher reflectivity (higher albedo) and in its turn less sunlight absorbed by the surface and the temperature decreases further. A negative feedback, i.e. dampening, could be when an increase in temperature leads to more water evaporating from the oceans and a higher concentration of water increases the cloud cover which can reflect sunlight and cool the Earth.

The drivers for climate change can both be natural and anthropogenic, i.e. human induced. The latest assessment report from the Intergovernmental Panel on Climate Change (IPCC) [3] shows that human activity over the past hundred years has had a large influence on the climate today. Increased levels of carbon dioxide are mainly due to the use of fossil fuels and agriculture has led to increased amounts of methane and nitrous oxide. These gases lead to a positive forcing and a surface temperature increase. Also the amount and distribution of aerosols, like sooth and dust, is dependent on human activity but result in a negative forcing which neutralizes the other factors a bit. The climate is thus very dependent on the atmospheric conditions. The composition of the atmosphere and the temperature affects the possible chemical reactions that can occur, which is of great interest in this work.

The total radiative forcing of a greenhouse gas depends on its ability to absorb infrared radiation, in which wavelengths it absorbs and its atmospheric lifetime, i.e. the time that the compound can be active as a greenhouse gas. When comparing the potential radiative forcing of 1 kg of one compound

with the forcing of 1 kg of a reference compound, usually CO_2, an index called the global warming potential (GWP) is obtained [1]. This is used to put different compounds on a relative scale, where the GWP for CO_2 is 1 and e.g. methane (CH_4) has a GWP of 296, and the Freon CFC-13 has 14 000.

1.2 Fossil fuels and other biofuels - environmental impact

The use of fossil fuels, which include coal, oil and natural gas, has been the main source of energy for industrial processes and vehicles since the industrial revolution in the 18th century. The concerns about climate change has led to interest in finding alternative ways to keep up the high living standard of today in the countries where the emissions of the greenhouse gases are the largest. For both environmental and economic reasons, efforts have been made in finding fuels that can be created from biomass, so called biofuels. Ethanol is a simple alcohol molecule (C_2H_6O) which is produced from sugar and biodiesel is esters which are produced from vegetable oil. Both of these are already in use, often in mixtures with regular gasoline or diesel. The disadvantage which competes with the lower emissions from the combustion is that the processes to create these fuels cost a lot of energy, and thus lead to carbon emission anyway. There is also a larger need for more land area to grow the plants to produce fuels, which can lead to emissions of e.g. methane. There might also be a competition between fuel production and other agricultural interests [4].

1.3 Furans

1.3.1 Chemical structure

Furans as chemical compounds are cyclic organics with five atoms building a ring structure, of which four are carbon atoms and one is an oxygen atom. The molecule called simply furan, C_4H_4O, has two double bonds and is shown in Figure 1.

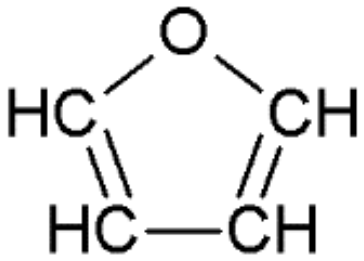


Figure 1. Chemical structure of furan, C_4H_4O.

The atoms are labeled from 1 to 5 starting with oxygen as number 1 and then increasing values counterclockwise. Other furan structures are molecules without double bonds, called tetrahydrofurans, which are of main importance in this work. In Figure 2a-d the chemical structure of furan and three types of tetrahydrofurans, some with additional methyl groups (-CH_3), are shown.

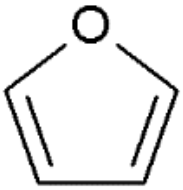
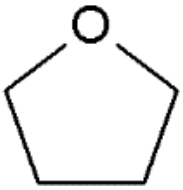
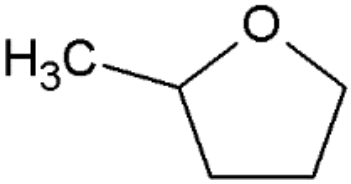


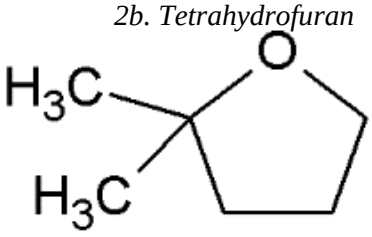
Figure 2a. Furan



2b. Tetrahydrofuran



2c. 2-Methyltetrahydrofuran



2d. 2,2-Dimethyltetrahydrofuran

In the rest of this work the molecules will be denoted furan (furan), THF (tetrahydrofuran), 2-MTHF (2-Methyltetrahydrofuran) and 2,2-DMTHF (2,2-Dimethyltetrahydrofuran) for simplicity.

1.3.2 Properties and areas of use

Furans are volatile organic compounds (VOCs) that are highly flammable both in liquid and gaseous phase. The liquids are colorless and the liquid 2-MTHF has a boiling point of 79 ºC. The boiling point of 2,2-DMTHF is not known but is expected to be somewhat higher than for 2-MTHF. Because of its properties it has been proposed as a new type of biofuel in combustion processes. It might then be possible to produce some furan derivatives from fructose through catalytic processes, but the technique has so far only been performed on a small scale. Potential large scale production is still only on a theoretical and planning stage. [6] The furans that have a higher energy density than ethanol are the most attractive when searching for new biofuels.

1.3.3 Environmental impact

Few studies have been made with furan derivatives, and especially the tetrahydrofurans. As the discussion about the furans potential as fuels has risen, the interest in its other chemical properties has also grown. The atmospheric chemistry is of great importance since it to a large extent determines whether the furans can be used as fuels at all. For example it is necessary to know if the effects of a large scale usage would be harmful for the environment or some life forms in any way. Compare e.g. with the usage of chlorofluorocarbons (CFC) which resulted in stratospheric chlorine and the annual ozone destruction, commonly known as the ozone hole, over Antarctica. The products from reactions with furans must also be investigated since usage as fuel for vehicles might result in smog scenarios if they are not easily removed from the air close to the ground.

The local, and finally global, environmental impact of a VOC depends on many factors, e.g. the abundance of compounds that the furan can react with, air pressure and temperature and also the weather and terrain features which affect the deposition, which is a sink in form of particles settling on surfaces. It is interesting to know what molecules that will form from reactions with furan, and also how fast the furans and their potential products will be removed from the atmosphere. One of the

largest sinks of furan derivatives will probably be reaction with the hydroxyl radical (OH·), which mostly initiates reactions with VOCs through hydrogen abstraction from a C-H bond. Chlorine atoms will also react with the furans in a similar way and provide a large sink in areas with a high enough Cl concentration.

1.3.4 Previous studies

At the time of writing there have been some studies, both experimental and theoretical, regarding reactions between furan derivatives and OH or Cl respectively. The studies have included reaction kinetics and, or, identification of products. The area is however not so well investigated that any standard values are available, and for compounds where there are more than one study available the results do not always agree. Some examples of furans that have been investigated with respect to OH reactions are 2- and 3-methylfuran, 2,3- and 2,5-Dimethylfuran [7] and furan [8]. Some examples of furans that have been investigated with respect to Cl initiated reactions are furan [9], [10], 2- and 3-methylfuran, 2-ethylfuran and 2,5-diethylfuran [10].

As mentioned in the previous section, the tetrahydrofurans have not been investigated experimentally to any large extension. There is a publication from 1990 by T. J. Wallington et al. [11] where α-Methyltetrahydrofuran (which is the same as 2-MTHF) was investigated with respect to OH reactions. The result was a considerably high atmospheric reactivity. Some other atmospheric implications of the furan derivatives that are not treated in this work are, high reactivity toward Cl, OH, NO_3 and also O_3 of which the reaction with Cl is the fastest. The lifetime of the furans in the atmosphere depends on the concentrations of the other reactants, which can vary a lot with time and location. All studies cited above agree that chlorine reactions might be dominant in marine and urban areas. No other known studies have included the 2-MTHF and 2,2-DMTHF molecules.

1.4 Objectives and question formulation

1.4.1 Aim of the project

All of the four furans, furan, THF, 2-MTHF and 2,2-DMTHF, need to be investigated but this project will focus on the last two. The aim at the beginning of this project was to investigate the two molecules 2-Methyltetrahydrofuran and 2,2-Dimethyltetrahydrofuran with respect to OH initiated reactions primarily, but also chlorine initiated reactions if there was time. Because of severe practical problems in the lab, the OH experiments were forced to be put aside at the beginning, and the work was instead focused on chlorine reactions. Due to lack of time there were no successful experiments performed with OH but instead the experiments with chlorine were more deeply investigated. This led to a change in the formulation of the questions with time, but since there are some previous studies of OH initiated reactions of furans available, these will be discussed as part of the project

By performing experiments, the rate constant for the reactions with Cl-atoms will be determined for both of the molecules respectively. The products from the reactions with Cl-atoms will be investigated and if possible, both the type of products and their amounts will be determined. A project will be performed in parallel where furan and tetrahydrofuran will be investigated, but this will only be included in the discussion parts of this report. The results from the experimental study, together with information from literature and previous studies in this area will be used to answer the questions below.

1.4.2 Questions to be answered

1a. What are the reactions rate coefficients for the two compounds 2-MTHF and 2,2-DMTHF against reactions with and Cl-atoms?

1b. How do these values compare with previous results for reactions with OH.

2a. What are the identifiable products from these reactions?

2b. How do the products from the Cl reactions differ depending on whether there is oxygen present or not? I.e. if the reaction takes place in N_2 or in an O_2/N_2 mixture.

3. How does the number of additional methyl groups affect the properties of the tetrahydrofurans?

4. How do these two compounds differ from those without methyl groups (furan and THF), including both the reaction rate constants and the product distribution?

5a. What can be concluded about the environmental impact, e.g. air quality, of these compounds on a local and a global scale?

5b. What is the GWP of the 2-MTHF and 2,2-DMTHF?

2. Theory

The basic chemical and physical principles needed to understand and to be able to perform the experimental part of the project are presented here. It includes some fact about the formation and atmospheric fate of the reactants that the furan will most probably react with in the atmosphere.

2.1 Chemical kinetics

The study of chemical kinetics includes determining the rate, i.e. the speed, of a reaction.[1] Knowing the speed of a chemical process is of major importance when determining the fate of a compound in the atmosphere; e.g. air pollution might be a result of slow kinetics.

Chemical reactions are divided into groups depending on their characteristics, for example the number of reactants. A first order reaction, or unimolecular reaction, is the type where one initial compound gives rise to two or more products which can be written generally as

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} \tag{2.1}$$

This could for example be decay processes and the reaction rate depends on the concentration of the compound A as

$$\frac{d[A]}{dt} = -k[A] \tag{2.2}$$

where k is called the rate constant and has the unit of s^{-1}. It is often convenient to talk about a compounds lifetime and it is obtained by rearranging and integrating equation (2.2),

$$\int \frac{d[A]}{[A]} = -\int k dt \tag{2.3}$$

which gives an expression that relates the initial concentration with the concentration after a certain time

$$\ln\left(\frac{[A]_t}{[A]_{t_0}}\right) = -kt. \tag{2.4}$$

The time it takes for the compound A to reach a value of $1/e$ of the original concentration, which is called the e-folding time and is a typical measurement of the lifetime (compare with half-life used typically in nuclear physics, where the concentration must reach half its original value). Since $\ln(1/e) = -1$ the atmospheric lifetime for the compound A is given as

$$\tau_A = \frac{1}{k}. \tag{2.5}$$

Spontaneous decay processes are however not that common in the atmosphere, but there are other first order reactions of greater interest. A very important atmospheric process is photo dissociation, where photons from the sun with certain wavelengths can induce this reaction

$$\mathrm{A} + h\nu \rightarrow \mathrm{B} + \mathrm{C} \tag{2.6}$$

where *hν* denotes the photon, whose energy is determined by the frequency, ν, or the wavelength, λ, as

$$E = h\nu = \frac{hc}{\lambda} \tag{2.7}$$

where *h* is the Planck constant. The photolysis rate constant is denoted j_A.

A reaction can also need a third body *M* to occur, i.e. a bath gas which can be the abundant air molecules N_2 or O_2,

$$\mathrm{A} + \mathrm{M} \rightarrow \mathrm{B} + \mathrm{C} + \mathrm{M} \tag{2.8}$$

which makes these reactions pressure dependent since the density of air molecules decreases with height above the mean sea level.

For a reaction with two compounds, i.e. a bimolecular reaction, which can be written generally as

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products}, \tag{2.9}$$

the reaction rate can be expressed as the change in concentration of one of the reactants with time, i.e.

$$\frac{d[A]}{dt} = -k[A][B], \tag{2.10}$$

where *k* is the rate coefficient for the specific reaction and has the unit molecule^{-1} cm^3 s^{-1}. For second order reactions, which is the reaction dealt with in this project, the lifetime is obtained in a similar way as for the first order reactions. Most often under atmospheric conditions the assumption can be made that [B] >> [A] if A is an atom or a radical and B is a molecule and thus the approximation

$$-k[A][B] \Rightarrow -k'[A] \tag{2.11}$$

is valid. Then equation (2.11) is integrated analogue to before with this assumption

$$\ln\left(\frac{[A]_{t_0}}{[A]_t}\right) = -k[B]_t = -k' \tag{2.12}$$

and the lifetime is then

$$\tau_A = \frac{1}{k'} = \frac{1}{k[B]} \tag{2.13}$$

which is equivalent to the first order reactions but it also depends on the concentration of the second reactant.

The kinetics can be applied in a similar manner for third order reactions which again includes one more reactant,

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{products}. \tag{2.14}$$

The rate constant is defined in the same way as before and the reaction rate relation can be written as

$$\frac{d[A]}{dt} = -k[A][B][C] \tag{2.15}$$

where *k* has the unit molecule^{-2} cm^6 s^{-1}.

A way to describe the reaction between two compounds in the atmosphere, particularly a radical A and a molecule BC,

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AB} + \mathrm{C} \tag{2.16}$$

is by the transition state theory. This assumes that the reaction has a short lived intermediate state which has a higher energy than both the reactants and the products see Figure 3.

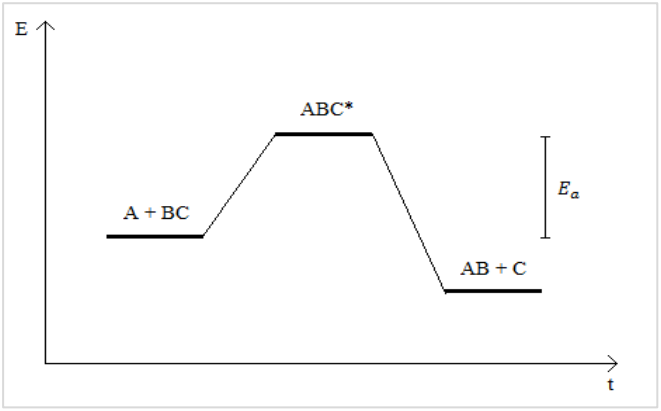


Figure 3. Intermediate state ABC in transition state theory. The potential energy of the molecules is shown as a function of time.*

This is called an activated complex and is denoted ABC*,

$$\mathrm{A} + \mathrm{BC} \rightleftarrows \mathrm{ABC}^* \rightarrow \mathrm{AB} + \mathrm{C}. \tag{2.17}$$

If the backward reaction is assumed to be preferred, the so called Arrhenius equation for the rate constant describes the rate of the reaction,

$$k = A \cdot \exp\left(\frac{E_a}{RT}\right) \tag{2.18}$$

where E_a is activation energy (see Figure 3), T is temperature, R is the gas constant with value 8.314 J $mol^{-1}K^{-1}$ and A is an experimental factor for the number of collisions. This expression explains how the rate changes with E_a and T and also if the reactions is exothermic or endothermic.

2.2 Halogen chemistry – Chlorine

Halogen is the common name of a group of elements along a column in the periodic table. These elements are similar in some ways because of their characteristic electron configuration which means that they miss one electron in the outer shell and thus halogens have high electronegativity. This makes them strong oxidizers, which means that they easily remove an electron from other compounds.

Halogens present in the atmosphere are chlorine, iodine and bromine. [12] These are partly emitted from the ocean surface in the form of sea salt, except for iodine which is released as gaseous iodocarbons from biochemical processes in the ocean. There is also a release of halogens into the atmosphere in the form of organic halogenated compounds from natural sources, but also from combustion of fossil fuels and industrial processes.

Because of the oxidation capacity of the halogens these can affect the tropospheric chemistry, especially in the marine boundary layer (MBL) which is the air closest to the surface above the oceans. Since more than 70 % of the earth's surface is covered with water the chemistry of halogens is important. The air is also continuously transported from sea to land and vice versa which makes both the chlorine from the MBL and the anthropogenic chlorine essential for e.g. coastal environmental chemistry. Figure 4 shows the total sodium deposition in the Nordic countries (the westernmost part of Norway is not covered by the model) which indicates the importance of sea salt for the coastal regions. [13] Since the sodium to a large extent comes from NaCl this map indicates that chlorine might have a similar spread. The reason for lower values around the Baltic Sea is due to its brackish water, which is not as salt as seawater.

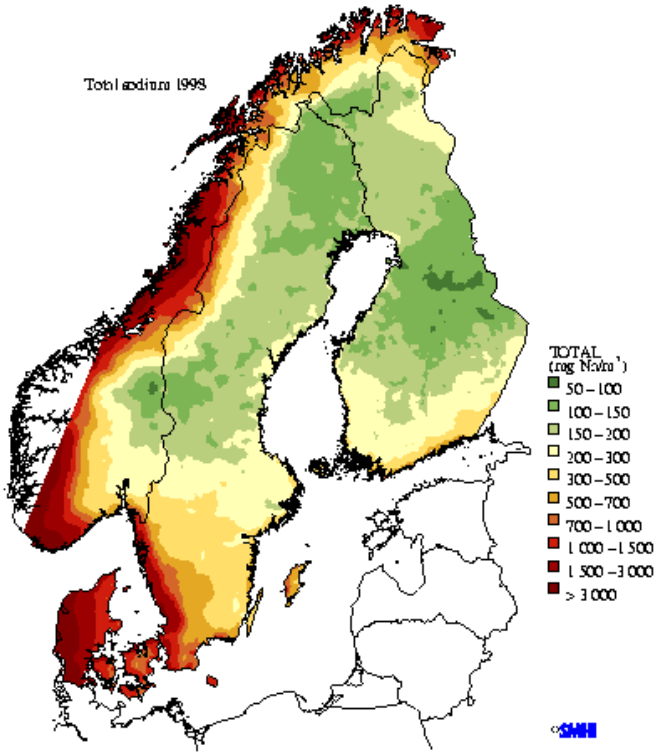


Figure 4. Mapping of base cations over the Nordic countries. The dataset was performed using the data assimilation part of the SMHI MATCH-model as of 2003 (optimum interpolation) with a grid spacing of 11km. [13]

Chlorine in the form of NaCl or other molecules is not very reactive so chlorine atoms have to be released for oxidation with atmospheric gasses to occur. One reaction path that releases chlorine atoms is the reaction between gaseous chlorine nitrate and sodium chloride in marine areas,

$$\mathrm{ClONO_2 + NaCl \rightarrow Cl_2 + NaNO_3} \tag{2.19}$$

and the Cl_2 is quickly photo dissociated into two chlorine atoms,

$$\mathrm{Cl_2} + h\nu \rightarrow 2\ \mathrm{Cl.} \tag{2.20}$$

The free chlorine atoms can react with ozone and then HO_2 in the troposphere, which result in that ClO and finally HOCl is formed through

$$\mathrm{Cl + O_3 \rightarrow ClO + O_2} \tag{2.21}$$

and

$$\mathrm{ClO} + \mathrm{HO_2} \rightarrow \mathrm{HOCl} + \mathrm{O_2}. \quad (2.22)$$

In the MBL Cl^- ions are present in sea salt particles and these can react with the HOCl molecule to form molecular chlorine,

$$\mathrm{HOCl} + \mathrm{Cl^-} \rightarrow \mathrm{Cl_2} + \mathrm{OH}\cdot, \quad (2.23)$$

which is photo dissociated in the same way as in (2.20).The net reaction is thus

$$\mathrm{Cl^-} + \mathrm{O_3} + \mathrm{HO_2} \rightarrow \mathrm{Cl} + \mathrm{OH}\cdot + 2\,\mathrm{O_2}. \quad (2.24)$$

It is important to notice that there is a net production of oxidizers (Cl and OH) in contrary to e.g. the reaction between OH and HCl where one OH radical is consumed while one Cl atom is formed. This reaction also shows that chlorine release results in a loss of ozone which can be an important process in both the troposphere and the stratosphere, resulting in e.g. the ozone hole over Antarctica [1]. The process for bromine release is similar.

The halogen atoms, predominantly Br and I, are very reactive towards ozone and will form oxygenated radicals, the reaction is

$$\mathrm{X} + \mathrm{O_3} \rightarrow \mathrm{XO} + \mathrm{O_2} \quad (2.25)$$

where X is Cl, Br or I. However, free chlorine atoms in the troposphere will react predominantly with one of the hydrogen atoms in the organic compounds. This can be either abstraction of hydrogen where HCl is formed, the reaction is

$$\mathrm{Cl} + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{HCl} \quad (2.26)$$

where R is some hydrocarbon. A substitution can occur where the chlorine and the hydrogen atom switch places, or if the organic contains double bonds there can also be an addition of chlorine atoms without forming any other product.

When Cl is released it can sustain a significant concentration, even though it reacts fast with many species in the atmosphere, because it is reformed in a catalytic cycle. Cl and ClO form the ClO_x family where the conversion between Cl and ClO is very rapid compared to the reactions that consume Cl and remove them from the cycle. This mechanism is mainly important when there is a significant amount of ozone present, which is needed to form ClO as in reaction (2.21). This could be in the ozone rich layer in the stratosphere or in polluted areas.

2.3 The hydroxyl radical – OH·

The hydroxyl radical, OH·, is an important atmospheric compound even though its concentration is less than one pptv (parts per trillion by volume) [5], but as a strong oxidant it is highly reactive towards many molecules. It acts as the major sink for many trace gases in the atmosphere since it does not react with the most abundant molecules O_2 and N_2, and it is therefore sometimes called "the garbage man of the troposphere"[1]. The primary source of atmospheric OH is the reaction of excited oxygen, $O(^1D)$, with water vapor.[1] For this to occur there must be sunlight since the formation process starts with photo dissociation of ozone.

[1] M. S. J. 2012

The possible products of this reaction are

$$O_3 + h\nu(< 319\ \text{nm}) \rightarrow O_2 + O \tag{2.27}$$

or

$$O_3 + h\nu(< 319\ \text{nm}) \rightarrow O_2 + O(^1D). \tag{2.28}$$

$O(^1D)$ cannot spontaneously decay to the ground state $O(^3P)$ because the transition between a singlet and a triplet state is forbidden. It is very likely that both the excited and the ground state atomic oxygen will collide with a bath gas molecule M, e.g. N_2 or O_2, within a short time and then the excited atom will deexcite by transferring its excess energy to M,

$$O(^1D) + M \rightarrow O + M \tag{2.29}$$

and the oxygen atoms will take part in the reformation of ozone,

$$O + O_2 + M \rightarrow O_3 + M. \tag{2.30}$$

This is a null cycle where no new molecules are formed, but if the $O(^1D)$ collides with a water molecule instead the product will be two OH radicals

$$O(^1D) + H_2O \rightarrow 2\ OH\cdot. \tag{2.31}$$

Most times the OH molecule reacts with VOCs through hydrogen abstraction to form water.

The OH radical is a part of the HO_x family together with HO_2 and its concentration is sustained in a similar way as for Cl atoms in the ClO_x family, mentioned in the previous section.

2.4 Beer-Lambert law

The amount of light that is absorbed when passing through a medium is related to the optical properties of the medium through Beer-Lamberts law [1], [14], which gives the absorbance as

$$A = \log\left(\frac{I_0}{I}\right) = \sigma N l \tag{2.32}$$

where I_0 and I are the intensities of the incident and the transmitted light respectively, σ is the absorption cross section, N is the number of molecules, i.e. the density, and l is the path length through the medium, see Figure 5.

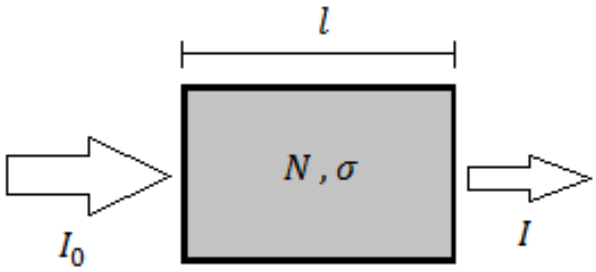


Figure 5. Beer-Lambert absorption.

This law gives that the fraction of light that is absorbed is independent of the incident light intensity but dependent of the number of absorbing molecules. The expression can also be written with wave length dependence,

$$\log\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sigma(\lambda)Nl. \tag{2.33}$$

E.g. if $I(\lambda) = I_0(\lambda)$ the absorption is: $A(\lambda) = \ln 1 = 0$, and the medium is completely transparent for the wavelength λ.

An infrared spectrum can be obtained in both transmittance and absorbance. The relation for transmittance is

$$T = \frac{I}{I_0} \tag{2.34}$$

where T ranges from zero to one representing complete absorption and no absorption respectively.

Thus the conversion between transmittance and absorbance is

$$A = -\log T. \tag{2.35}$$

So $A = 0$ equals no absorption, $A = 1$ equals 90 % absorption, $A = 2$ equals 99 % absorption and so on, in contrary to transmission where $T = 0$ means full absorption and $T = 1$ means zero absorption.

2.5 Molecules and IR-spectroscopy

2.5.1 Molecular spectra

Not all media are transparent to all types of electromagnetic radiation, i.e. different wavelengths. For example gases in the atmosphere like H_2O, CO_2 and CH_4 will let the relatively short wavelengths of the visible sunlight trough, but infrared radiation from earth will get absorbed. The reason for the greenhouse effect, and why different compounds can absorb and emit in different wavelengths in general, lies in atomic and molecular physics. [15]

Electrons will feel an attractive force from another nearby atom, and a repulsive force from the other electrons. If the electrons are rearranged when to atoms are approaching each other, so that the net force is attractive a bound state with more than one atom is created, i.e. these atoms will form a molecule. If a certain amount of energy is added to the system corresponding to the binding energy of the molecule, the molecule can dissociate into free atoms again, e.g. dissociation of O_2 by UV-light (~10-400 nm, [16]) in ozone formation. But if the molecule is exposed to a photon with lower energy, e.g. ozone with infrared radiation (~700 nm-1mm, [16]), the energy might transfer and result in an excitation of the molecule instead. The energy needed to excite an atom or a molecule is not continuous but has discrete values which are determined by the properties of the compound. This makes it possible to identify molecules with IR-spectroscopy since different molecules will absorb in different wavelengths and a spectrum with characteristic absorption lines is obtained.

The molecule is rather complex when it comes to its excited states since the energy of a molecule is described by an electronic energy, a vibrational energy and a rotational energy. All these energies contribute to the total energy of the molecule. All the different types mentioned can be in different energy states described by quantum mechanical relations and the selection rules for which transitions

that are allowed also arises from quantum mechanics. The spacing between the energy states for the three types differs in many orders of magnitude, where rotational states have the smallest spacing and the electronic states the largest. It can be pictured as the rotational states being the fine structure of the vibrational, which in its turn is the fine structure of the electronic state.

The uniqueness in absorbance of each molecule arises because different elements have different nuclear mass which, among other things, affects the distance between the nuclei and between the electrons. The molecule can vibrate and rotate with respect to its center of mass which is dependent on the atoms that build up the molecule.

Different energies are needed for different excitations, e.g. a pure rotational energy transitions within the same electronic state is achieved in the relatively low energetic microwave range (~1 mm-15 cm, [16]) while transitions between different electronic states occur in the near infrared, the visible (400-700 nm) or the UV region. The transitions induced by infrared radiation are rotational-vibrational transitions. Due to the energy spacing for the rotational and vibrational states described before, the rotational structure turns the vibrational transitions to bands which give a characteristic pattern in the infrared spectrum with equidistant peaks around a center with no peak. The molecular infrared spectra are thus rich in lines but show a very systematic and regular behavior, which makes them not so much harder to identify than atomic spectra. However, the fine structure of a molecular spectrum is most pronounced for smaller molecules. For larger molecules the peaks are more smeared out and the fine structure melts together to a broader peak because of the larger number of possible interaction between the atoms in the molecule. See Figure 6 for an example of a typical IR spectrum of a small molecule, in this case carbon dioxide

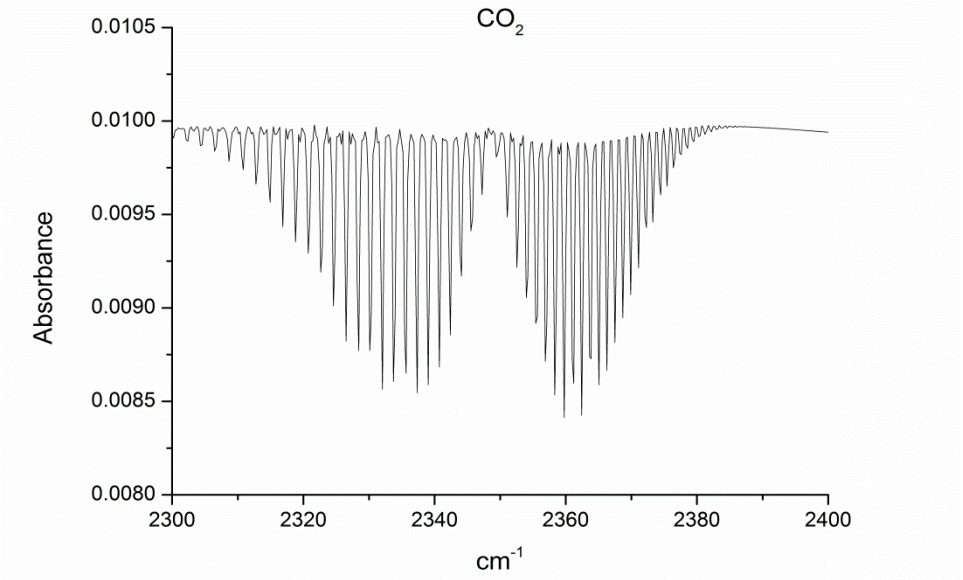


Figure 6. Absorbance spectrum for CO_2 in the IR wavelength region.

2.5.2 Characteristic group frequencies

Even though the whole molecule can vibrate, the vibrations of the individual bonds are to some approximation determining for the spectrum characteristics [14]. Some types of vibration are bending, stretching (symmetric and asymmetric), rocking and twisting. A specific type of chemical bond between two specific atoms is generally found in a limited absorption frequency, or wavenumber, region, called a band. Since all the atoms in a larger molecule are affected by each other there is no discrete frequency for one bond type which is common for all different molecules, but there is rather

this characteristic range. Knowledge about the typical absorption frequencies for a functional group is an important guidance when studying absorption spectra. Some approximate absorption frequencies for characteristic groups are shown in Table 1.

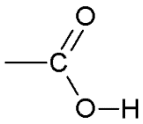
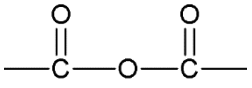
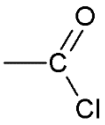
Group	Name	Band
	Carbonyl	1850-1700 cm^{-1}
	C-H Stretch	3000-2700 cm^{-1}
	Saturated carboxylic acid	1725-1700 cm^{-1} 3000-2500 cm^{-1}
	Acid anhydrides	1800-1850 cm^{-1}
	Acid chlorides	1815-1790 cm^{-1}

Table1. Absorption frequencies of characteristic bonds.

2.5.3 FTIR

Fourier transform infrared spectroscopy (FTIR) is based on the concept that a sample of gases absorb IR light at some wavelengths and let some of it through unaffected. A beam of light with wavelengths covering almost the whole IR range is sent through a beam splitter which divides it into two beams, with half the initial intensity [14]. One of the beams is sent through the sample, and is thus absorbed at some wavelengths before reaching the detector, and the other beam goes directly into the detector. It is also possible to let both the beams go through the sample provided that one on them travels a longer path before reaching the detector. These two beams will then recombine and create an interference pattern for all the wavelengths at the same time, i.e. a sum of interference patterns for each wavelength respectively. The difference between the path lengths of the two beams can be changed systematically by moving the optics and the final signal will vary with the path difference and the detector will give out a signal in the form of an interferogram. A computer connected to the detector makes a Fourier transform of the signal and creates a spectrum with absorption as a function of wavenumber, which can then be analyzed. The main advantage of FTIR is that all wavelengths can be analyzed at the same time and in relatively short time intervals.

3. Method

In this project, all the experiments were performed in a photochemical reactor at the Copenhagen Centre for atmospheric research. [17] The reactor basically consists of a quartz glass tube surrounded by different lamps, and it is connected to a FTIR (Fourier Transform Infrared) spectrometer. This instrument can be used to imitate and study the chemistry in the atmosphere, since both the speed and the products of photolysis induced chemical reactions can be determined under atmospheric conditions. The methods used to perform the experiments as well as to analyze the results are presented here.

3.1 Instrument – The photochemical reactor

A sketch over the experimental assembly with its main parts is shown in Figure 7.

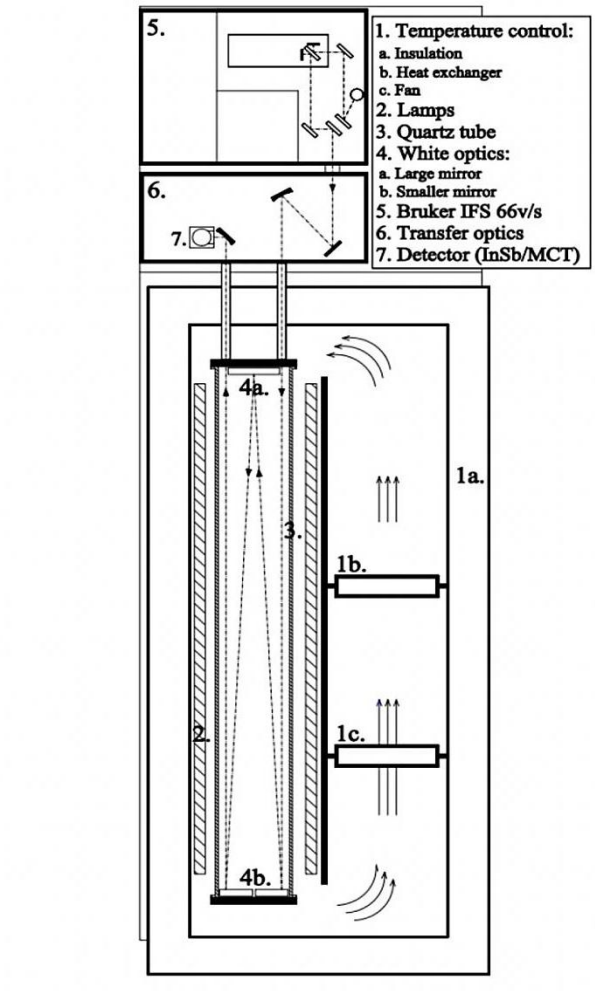


Figure 7. The main components of the photochemical reactor. [17]

The quartz glass reaction chamber is a 2m long cylinder with a volume of 100 liters connected to a gas inlet system and a vacuum pump to empty the chamber. A temperature control system allows determining the temperature in the chamber, in these experiments the temperature was set to be 25 ºC. This temperature is the standard value for room temperature and thus chosen for simpler comparison with results from other experiments. To get a gaseous compound into the chamber it is first introduced

into a small container of 144.2 ml outside the chamber enclosure. The connection between the small volume and the reaction chamber can be closed and two pressure gauges are connected to one of the volumes respectively. The volume conversion factor between the small introduction volume and the chamber is ca. 693. In most of the experiments the gasses were introduced when there was a vacuum in the chamber, i.e. they were sucked into the reaction chamber due to the pressure difference. If the pressure in the reaction chamber is the same as, or larger than, the pressure in the small container, it is also possible to push a gas into the reaction chamber with a flow of N_2. The gasses enter the chamber via many holes distributed along the gas inlet tube to get a good mixture.

The lamps surrounding the chamber are 8 UV-A lamps, with a wavelength range of 325-380 nm, 16 UV-C lamps, with the wavelength 254 nm and 12 sunlight lamps with a broad wavelength range from about 300 nm up to infrared light. The number of lamps used and the photolysis time can be controlled through a computer program. All lamps are turned on and off manually, which makes the photolysis time approximate, especially for very short intervals.

The infrared beam from the FTIR interferometer can go through the chamber many times due to an optical system with adjustable gold coated mirrors in both ends of the quartz glass cylinder. In these experiments an optical path way of 64 m was used. The detector used was a MCT-detector which was cooled with liquid nitrogen.

3.2 Measurements

3.2.1 Different types of experiments

This work includes a variety of experiments with different aims and small differences in procedure. The two major types of experiments are product studies and relative rate studies, which were performed for both 2-MTHF and 2,2-DMTHF respectively. All the experiments have in common that the first spectrum is of an empty chamber, i.e. vacuum, and the second is a background spectrum with only nitrogen or technical air respectively. After that, different constellations of reactants together with N_2 or an O_2/N_2 mixture can be investigated and the spectra can be divided with the background spectra from before to get a clearer visual presentation. For each new mixture a spectrum is taken both directly after the compounds have been inserted and also after waiting five minutes, to make sure that no reaction occurs in the dark. All experiments are performed under atmospheric conditions, i.e. a temperature of 25 ºC and a pressure close to 980 mbar, and are reproduced once to confirm the results.

In the product studies the only reactants are the furan and the chlorine atoms. After photolysis the spectrum can tell where the products have their largest infrared absorption and conclusions can be drawn about what kind of products that will form when a furan reacts with chlorine atoms in the atmosphere.

To determine the reaction rate of the reactions between a furan and Cl atoms, a second type of experiment is performed. The relative rate experiments have an additional compound that also reacts with Cl, called a reference compound. The two reference compounds used are ethylene, C_2H_4, and ethane, C_2H_6. The reason for using both C_2H_4 and C_2H_6 is to confirm that the rate coefficient becomes the same for the reaction (3.1) independently of which reference compound that is used in the experiment. After a number of photolysis steps the gradual decrease in concentration of the furan and the reference compound respectively, can be compared and a rate coefficient can be determined using the relative rate method.

3.2.2 The relative rate method

The relative rate method is a way to determine the reactivity, i.e. the rate constant, of e.g. a volatile organic compound (VOC) like the furans with a radical like the OH molecule or Cl atoms [7]. It is based on the comparison between the compound of interest and a reference compound, which are both let to react with the same radical. Using a reference compound which has a well-known rate coefficient for the reaction against the radical makes it possible to calculate the unknown rate coefficient for the furan. The condition for this method to be valid is that neither the furan nor the reference compound reacts in any other way than with the radical, and also that neither of these compounds is produced in any other chemical process. The relative rate method is general and can be used for any reaction obeying the conditions, taking for example the reaction between furan and chlorine atoms

$$\text{furan} + \text{Cl} + h\nu \rightarrow \text{products} \tag{3.1}$$

$$\text{reference} + \text{Cl} + h\nu \rightarrow \text{products}. \tag{3.2}$$

The free chlorine atoms are obtained through photo dissociation which also occurs in UV light, see reaction (2.20).

Using Equation (1), the change of concentration with time is

$$\frac{d[\text{furan}]}{dt} = -k_f[\text{furan}][\text{Cl}] \tag{3.3}$$

and

$$\frac{d[\text{reference}]}{dt} = -k_r[\text{reference}][\text{Cl}]. \tag{3.4}$$

Since [Cl] is the same for both of the equations with time, the expressions can be related as

$$\ln\left(\frac{[\text{furan}]_{t_0}}{[\text{furan}]_t}\right) = \frac{k_f}{k_r}\ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right). \tag{3.5}$$

For each experiment there are eleven concentrations, including the one at t = 0 which is the initial concentration. If $\ln([\text{furan}]_{t_0}/[\text{furan}]_t)$ is plotted against $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ for each of the photolysis steps, it should yield points lying on a straight line. The line fitted to the points should intersect the origin and have the gradient

$$k_g = \frac{k_f}{k_r}. \tag{3.6}$$

With the value for k_2 known, the rate coefficient for the reaction between the furan and chlorine is simply

$$k_f = k_g \cdot k_r. \tag{3.7}$$

3.2.3 Procedure

When introducing gases to the reaction chamber the compound of interest is first prepared in a glass flask with one opening and an air tight sealing. 2-MTHF and 2,2-DMTHF are liquids at room temperature and approximately one centiliter is poured into a flask with a volume of approximately half a liter. The furans are volatile enough to fill the flask with gas and no liquid is introduced into the gas inlet system. Before using the 2-MTHF and 2,2-DMTHF, these are purified by freezing the sample and putting the flask in liquid nitrogen. When the sample is solid the flask is connected to a vacuum pump to extract potential contaminations. This procedure is repeated three times. The gaseous compounds are filled into the glass flasks by an authorized person at the CCAR. The prepared glass flasks can then be easily attached to, and removed from, an opening in the gas inlet system. It is of major importance to pump out all the air that is in the connection part after switching sample since this is not wanted in the reaction chamber.

The first experimental measurement that has to be done is to create a reference spectrum for each of the furans to be investigated, and also the compound C_2H_6 which is used as a reference in some experiments. A specific amount of 2-MTHF, 2,2-DMTHF or C_2H_6 is introduced followed by filling up with N_2 to approximately 980 mbar and then a spectrum is taken, see Table 1. For the reference spectra the settings were a resolution of 0.2 cm^{-1} and 128 scans. For the reference spectra it is important to know the initiated concentration since this is used as an input parameter for the analysis program later.

For product studies with chlorine the different furans were initiated with different concentrations together with Cl_2 and N_2, see Table 1. The amount does not have to be known exactly since the analysis of the spectra will provide the concentrations of the compounds in the chamber. It is however good to have an approximate idea of how much that is initiated since good spectra are necessary and if the experiment needs to be repeated it is possible to change the amounts in a good way. An excess of chlorine is desirable because it is only the reaction with Cl atoms that is of interest and if it is not present other reactions will start to take place. Therefore a partial pressure ten times greater than the partial pressure of the furan was used. The mixture was then photolysed in ten steps with a photolysis time of approximately one second in the beginning, and then successively longer steps of two up to five or ten seconds to make sure that all the furan reacts. Waiting for two minutes after each photolysis makes sure that the initiated chemistry is allowed to fully proceed. After each photolysis a spectrum with a resolution of 0.5 cm^{-1} and 32 scans was taken.

The relative rate studies were performed in a similar way as the product studies, but before filling up with N_2 the reference compound was also initiated. The amounts of 2,2-DMTHF or 2-MTHF and the reference compound vary a little bit but are in the same order of magnitude and result in approximately 10 ppm in the reaction chamber. It is however not important to have the same amount of the furan and the reference since only the relative change is of interest in these experiments. For both of the furans very short photolysis time is needed; each step represents a maximum of one second of photolysis. The spectra were taken after two minutes and had a resolution of 0.5 cm^{-1} and 32 scans.

For all experiments with chlorine a short photolysis time with only one UV-A lamp is used. These small intervals of light are necessary because of the high reactivity of the furans and to be sure not to photolyse all at once, but to be able to do it in many steps. The concentrations used in the different experiments are shown in Table 2.

3.3 Tables of experiments

The concentrations used for all individual compounds in each experiment are shown in Table 2-6 below. The tables also include the total pressure in the reaction chamber after filling it with nitrogen (or technical air) and the number of photolysis steps. Table 2 presents the concentrations for the reference spectra, Table 3-4 presents the concentrations for the experiments with Cl reactions and Table 5-6 for the product experiments. Values marked with * indicate that the uncertainty for the value is larger because the insertion method was a bit different.

Initiated compounds	Partial pressures in reaction chamber/10^{-3} mbar	Total pressure/ mbar
2-MTHF	14.0	978
2,2-DMTHF	6.06	979

Table 2.Values for the concentrations and total pressure, used for the reference spectra of 2-MTHF and 2,2-DMTHF.

Initiated compounds	Partial pressures in reaction chamber/10^{-3} mbar	Total pressure/ mbar	Photolysis steps (each of ~1s)
2-MTHF **C_2H_4** **Cl_2**	14.4 15.9 78.2	973	2
2-MTHF **C_2H_4** **Cl_2**	17.3 16.7 89.8	979	10
2-MTHF **C_2H_6** **Cl_2**	16.9 14.9 216*	969	5
2-MTHF **C_2H_6** **Cl_2**	15.6 18.6 74.3	979	10
2MTHF **C_2H_6** **Cl_2**	12.0 21.2 111*	978	8
2MTHF **C_2H_6** **Cl_2**	8.6 5.8* 119*	980	10

Table 3. Concentrations and total pressure used in the experiments with 2-MTHF and Cl.

Initiated compounds	Partial pressures in reaction chamber/10^{-3} mbar	Total pressure/ mbar	Photolysis steps (each of ~1s)
2,2-DMTHF **C_2H_4** **Cl_2**			7
2,2-DMTHF **C_2H_4** **Cl_2**			10
2,2-DMTHF **C_2H_6** **Cl_2**	43.0 14.3 218	980	4
2,2- DMTHF **C_2H_6** **Cl_2**	15.3 15.9* 74.6	970	8
2,2- DMTHF **C_2H_6** **Cl_2**	13.6 14.7 143	980	5

Table 4. Concentrations and total pressure used in the experiments with 2,2-DMTHF and Cl. The values missing were not recorded during the experiment but are similar to those in the last row.

Initiated compounds	Partial pressures in reaction chamber/10^{-3} mbar	Total pressure/ mbar	Photolysis steps (each of ~1s)
2-MTHF **Cl_2** **N_2**	13.0 75.8	972	6
2-MTHF **Cl_2** **N_2**	8.7 154	980	10
2-MTHF **Cl_2** **N_2/O_2**	10.0 196*	983	10

Table 5. Concentrations and total pressure used in the experiments product studies with 2-MTHF.

Initiated compounds	Partial pressures in reaction chamber/10^{-3} mbar	Total pressure/ mbar	Photolysis steps (each of ~1s)
2,2- DMTHF **Cl_2** **N_2**	12.7 155*	978	10
2,2- DMTHF **Cl_2** **N_2/O_2**	16.0 215*	977	11

Table 6. Concentrations and total pressure used in the experiments product studies with 2,2-DMTHF.

3.4 Analysis

3.4.1 Use of analysis programs

For the analysis the two programs *OPUS* and *MALT5* were used. *OPUS* is used to set the parameters for the data sampling, e.g. resolution, number of scans, file format, file name etc. When a measurement is completed the spectrum will be shown visually in *OPUS* and the program allows modifying the spectrum, e.g. subtract the background spectrum and change color and range for a clear and pedagogical visual presentation and a first rough analysis.

MALT5 (Multi-Atmospheric Layer Transmission 5) is a program that simulates and fits infrared spectra to measured ones. [18] It calculates the transmission, absorbance or emission spectrum and fits a new spectrum using parameters from the *HITRAN* database [19] and by iterating it until the mean-square residual is minimized, i.e. until the best possible fit. From the information about e.g. temperature dependence in the *HITRAN* database, *MALT5* will calculate the current absorption of a compound adjusted for the temperature used in the experiment. It is also possible to add reference spectra for compounds that are not in *HITRAN*, e.g. 2-MTHF and 2,2-DMTHF and set the information about temperature, pressure and concentration to be used. The synthetic, fitted spectrum is then used to make a quantitative analysis of the concentrations of the compounds in the sample. Since the concentration in each of the reference spectra used to create the fit is known, the program will provide a concentration for each compound analyzed. It is possible to fit spectra with more than one substance and to overlapping spectral lines.

A text file was created for *MALT5* to read. In this file, all the necessary data about the experiment as pressure, temperature, path length and what region of the spectrum to analyze was set and the different compounds to be included in the analysis was chosen. If possible it is preferable to choose an analysis region which extends beyond the absorbance lines of the compounds, since a reference base line simplifies the fitting. The reference spectra used for 2-MTHF and 2,2-DMTHF were the measured ones described in the previous section, see also Figure 8 and 9. The reference spectra for one reference compound and for some products were taken from the HITRAN database, number 1 for H_2O, 2 for CO_2, 5 for CO, 15 for HCl and 38 for C_2H_4, [19].

The procedure to get a good synthetic spectrum includes a first good guess of the parameter values. This includes the concentration in ppm, the shift of the curve along the wave number axis and the field of view (FOV). The easiest way to adjust these values is to keep all but one invariable and let the program be able to change this value. If the spectrum looks better with the value chosen by *MALT5*, the parameter can be changed to this value and a new parameter is varied. This is repeated until the lowest error is achieved. When a good fit is available for the first spectrum in a series the same parameters are used for the rest of the spectra in the same series as well.

The output from *MALT5* is the original spectrum, the spectrum fitted by the program and the residual spectrum, i.e. the difference between the measured and the fitted. From the residual spectrum it is possible to say whether the program has done a good fit or not and if the simulation is trustworthy enough to use. For almost all spectra there will be some spectral lines from water present in the region 1400-1700 cm^{-1}, see e.g. between 1450 cm^{-1} and 1600 cm^{-1} in Figure 10. This is due to that it is almost impossible to get rid of all the water vapor even if the vacuum pump is good. This results in a small amount of water in the background spectrum, and when the rest of the spectra are divided with this the result is an appearance of negative water concentrations. Since this is a known fact, these spectral lines can be ignored in the analysis.

For the experiments consisting of a series of measurements it is possible to create a list where *MALT5* can read e.g. all the ten photolysis steps. The output will then be a list of the concentrations for the compounds investigated.

3.4.2 Relative rate analysis

If the absorption spectra of the furan and the reference compound overlap and are hard to analyze at the same time, it is possible to analyze them in separate regions. It is also good if you can confirm the analysis by getting the same result when looking at two different regions for the same compound. The relative rate spectra can be analyzed even if all the products are not known, which is the case for 2-MTHF and 2,2-DMTHF. As long as the unknown products are not affecting the fitting of the furan and the reference, it does not matter if it is visible in the residual absorbance spectrum since its presence can be explained. If possible, a region without product accumulation can be chosen for analysis.

For the relative rate experiments, the list of data with concentration changing with photolysis time is recalculated with equation (3.5) and the values for the furan is plotted against those for the reference compound. The data points will produce a straight line for approximately the five first photolysis steps. After that other chemistry will play a larger role since the furan and references reaches critically low concentrations. The last data points that diverge from the straight line will not be used in the linear regression. Finally the rate constant for 2-MTHF and 2,2-DMTHF can be calculated respectively. The rate constants used for the reference compounds are: $k_{C2H4} = 9.29 \cdot 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ for C_2H_4, and $k_{C2H6} = 5.70 \cdot 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ for C_2H_6 [20].

3.4.3 Product analysis

The current analysis of the product experiments includes obtaining the change in concentrations with photolysis time for the furan and the known products from the synthetic spectra. The known products include HCl, CO_2, CO and H_2O, where the last three are predominantly present in the experiments performed with N_2/O_2 mixture. Attempts at identifying the unknown products are done by identifying the characteristic groups (see Table 1) and comparing the measured spectra with existing spectra for the simpler probable products. There are not spectra available for all the possible chlorinated products so only qualified guesses can be made about their properties.

4. Results

The results from the experimental work and the analysis will be presented as diagrams and tables. A short explanation is provided for each figure or table but the interpretation and conclusions will be presented in the next chapter. A few illustrative examples are also presented to show e.g. good and bad analyses.

4.1 Reference spectra for 2-MTHF and 2,2-DMTHF

The first part of the experimental work included creating reference spectra for the two furans. Figure 8 and 9 show the reference spectra used in the analysis, with 14.3 ppm 2-MTHF and 6.20 ppm 2,2-DMTHF respectively. Figure 11 shows the measured spectrum of the reference compound C_2H_6, with a concentration of 37.8 ppm.

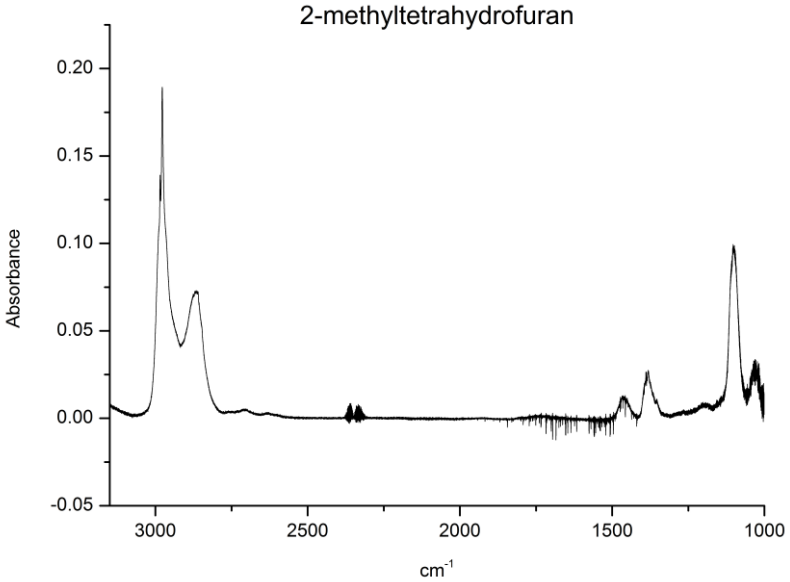


Figure 8. Reference spectrum of 2-MTHF.

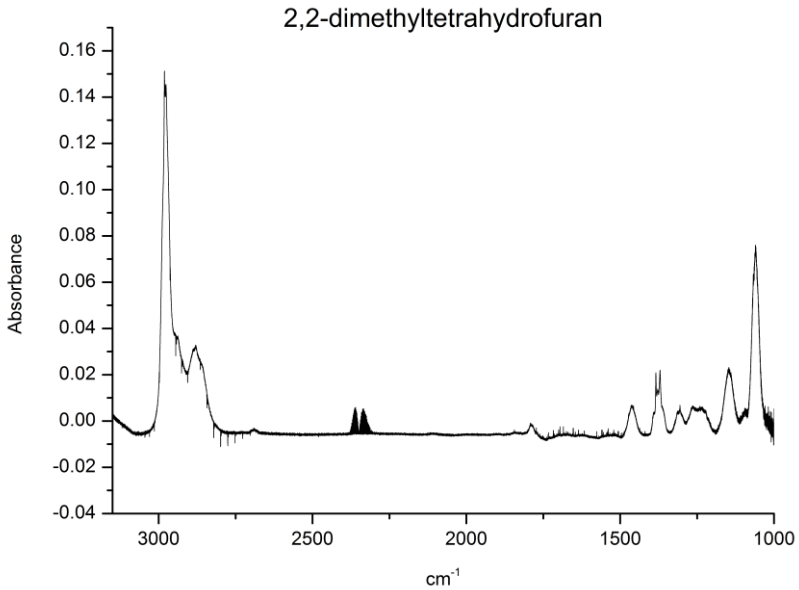


Figure 9. Reference spectrum of 2,2-DMTHF

There are some features in the reference spectra in Figure 8 and 9 that do not belong to the furans but are traces of other molecules that are hard to get rid of in the reaction chamber. The two compact "bumps" around 2300 cm^{-1} belong to CO_2 and the small peaks between 1500 cm^{-1} and 1800 cm^{-1}, that also might be negative, belong to H_2O. These are present in all the spectra but in so small amounts that it does not affect the experiments or the analysis.

4.2 Relative rate experiments

For the rest of the results, chlorine atoms are always included in the samples. Waiting five minutes after initiating the compound did not result in any visible changes in the spectra, neither for 2-MTHF or 2,2-DMTHF. This concludes that the reactions between the furans and chlorine without the presence of UV-light are negligible. For the relative rate experiments there were four successful results for each of the compounds. Before calculating the rate coefficient a good fit is needed for the first spectrum in a photolysis series. Figure 10 shows a typical example of a good fit where the features of the spectrum have been captured by the program. In this interval of the spectrum the most intense peak of the 2-MTHF is visible at 1100 cm^{-1} and the reference is seen in 1400-1500 cm^{-1}. In the residual there is almost exclusively water lines that are off from the otherwise straight line.

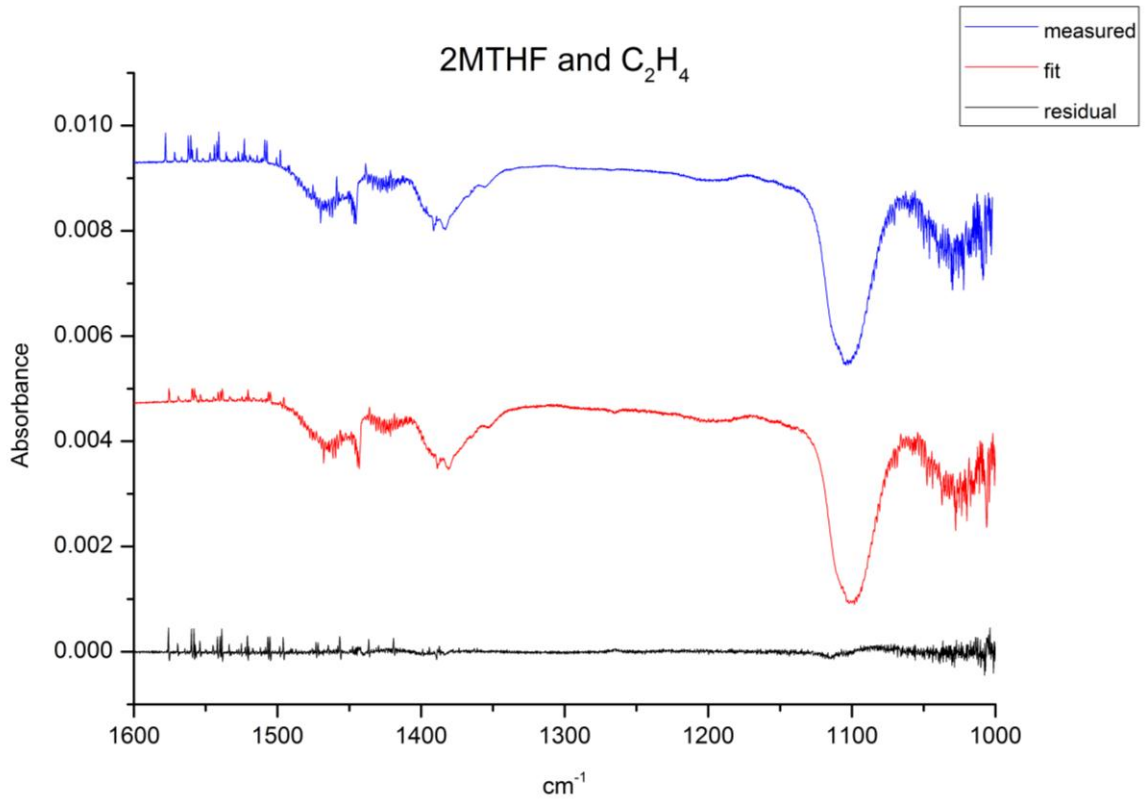


Figure 10. Example of a good analyzed spectrum with measured, fitted and residual spectrum in the same picture.

It is also visible from Figure 10 that the signal to noise ratio for this experiment is very high, which is an indication of good quality spectra. This is in common for all of the experiments.

There are regions where the absorbance peaks of the reference and the furan overlap a lot more than in Figure 10. This is the case for C_2H_6 which has its most significant peak in 2800-3100 cm^{-1}, i.e. the same as the furans, see Figure 11.

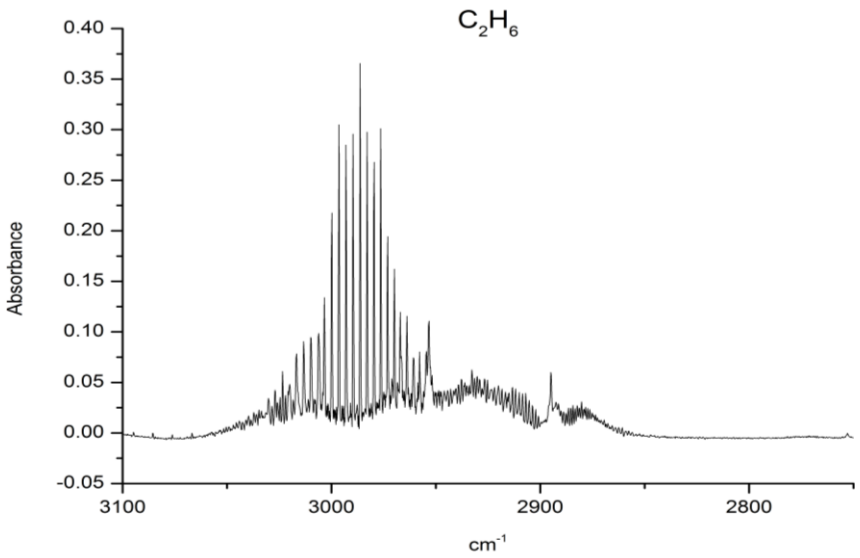


Figure 11. The most significant structure in the IR-spectrum of the reference compound methylene, C_2H_6, in the region around 3000 cm^{-1}.

This region is preferred in the analysis since there is a lot less products forming here than in 1000-1600 cm^{-1}. It is however possible for *MALT5* to distinguish the features of the compounds respectively and create a good synthetic spectrum. If the analysis is difficult to do for two compounds at the same time, especially for the following photolysis steps, they can be analyzed one at a time. Then the features of the compound not analyzed will be observable in the residual, which indicates that the program has ignored this structure as wished. An example is seen in Figure 12, where a sample with 2,2-DMTHF and C_2H_6 is analyzed for the 2,2-DMTHF only and the characteristic shape of the C_2H_6 is seen around 3000 cm^{-1} in the residual spectrum.

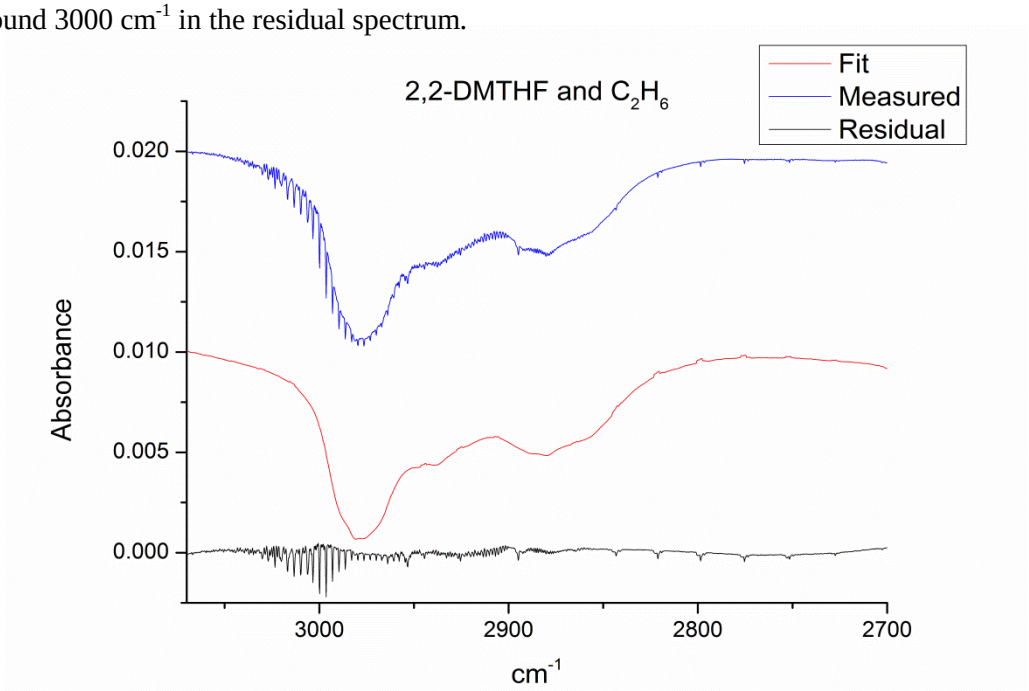


Figure 12. Analyzed spectrum in the range 2700-3070 cm^{-1} where both the 2,2-DMTHF and the reference C_2H_6 are present but only the 2,2-DMTHF is fitted.

Sometimes it is necessary to use a much smaller interval when analyzing the reference compounds C_2H_4 and C_2H_6 just because of their overlap with both the furans but also with the peaks from the product HCl, which are present in the same region. An example of this is shown in Figure 13 which is from the same experiment as Figure 12.

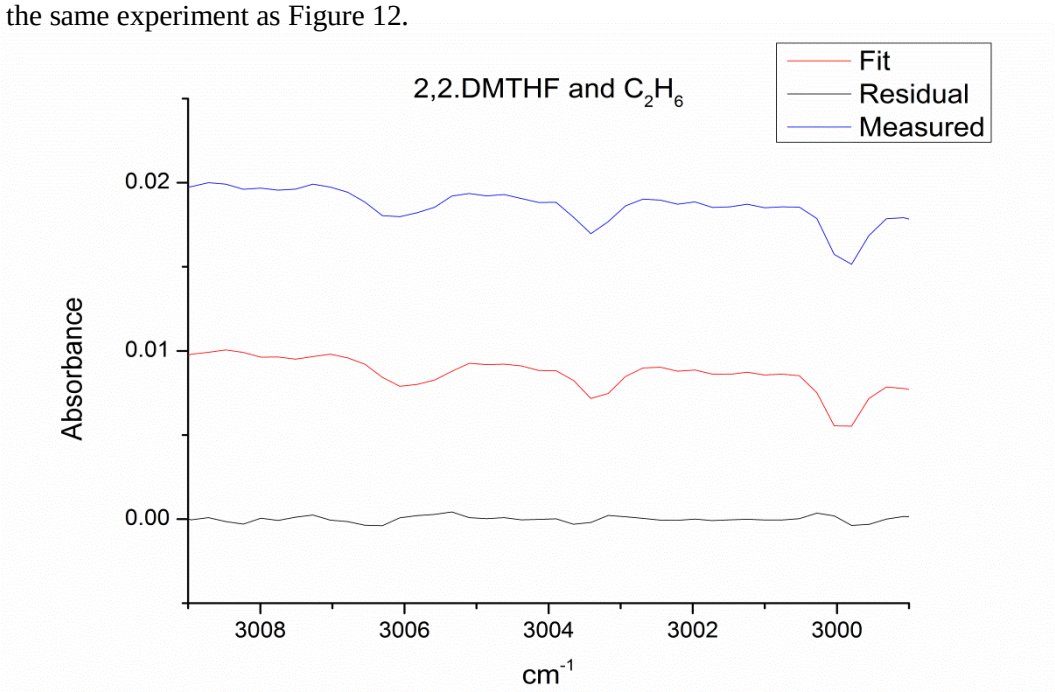


Figure 13. Analyzed spectrum in the range 2999-3009 cm^{-1} where both the 2,2-DMTHF and the reference are present but only the C_2H_6 is fitted.

Figure 14 shows an example of when the program has problems with creating a reliable fit to the measured spectrum. This was often the case for spectra after a couple of photolysis steps. Figure 14 represents a sample that has been photolysed for about three seconds.

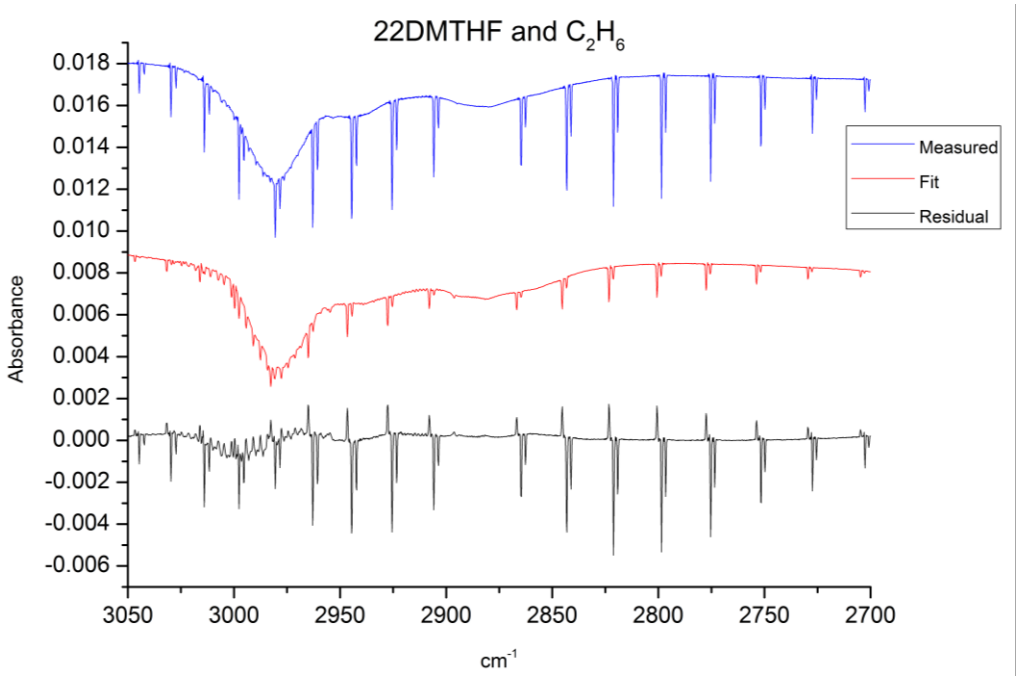


Figure 14. Example of a bad analyzed spectrum with measured, fitted and residual spectrum in the same picture. The experiment was with 2,2-DMTHF and C_2H_6.

The reference, which is seen as the small equidistant peaks on top of the curve of the 2,2-DMTHF between approximately between 2950 cm^{-1} and 3050 cm^{-1}, is captured but with a higher amplitude than expected and the intense narrow peaks appearing in pairs, belonging to HCl are shifted, which creates a completely wrong fit. This results in a residual spectrum with many negative lines, and is not optimal as a basis for calculating the rate coefficient. However, the HCl does not need to be analyzed to get a value for the rate constant, so the best possible fit to each reference compound and furan was the ultimate aim of the analysis.

The final result of the relative rate experiments is, as mentioned before, a data set with a linear regression. All the obtained plots are shown in Figure 15-18 below. No error bars are indicated in the figures but this does not necessarily mean that the error is very small. The largest error probably lies in the analysis, but the output from the program shows unreasonably small errors of only fractions of a percent. It is clear from the figures below that the spread is larger than that and it is recommended to look at the distribution of the data points to get an estimation of the error.

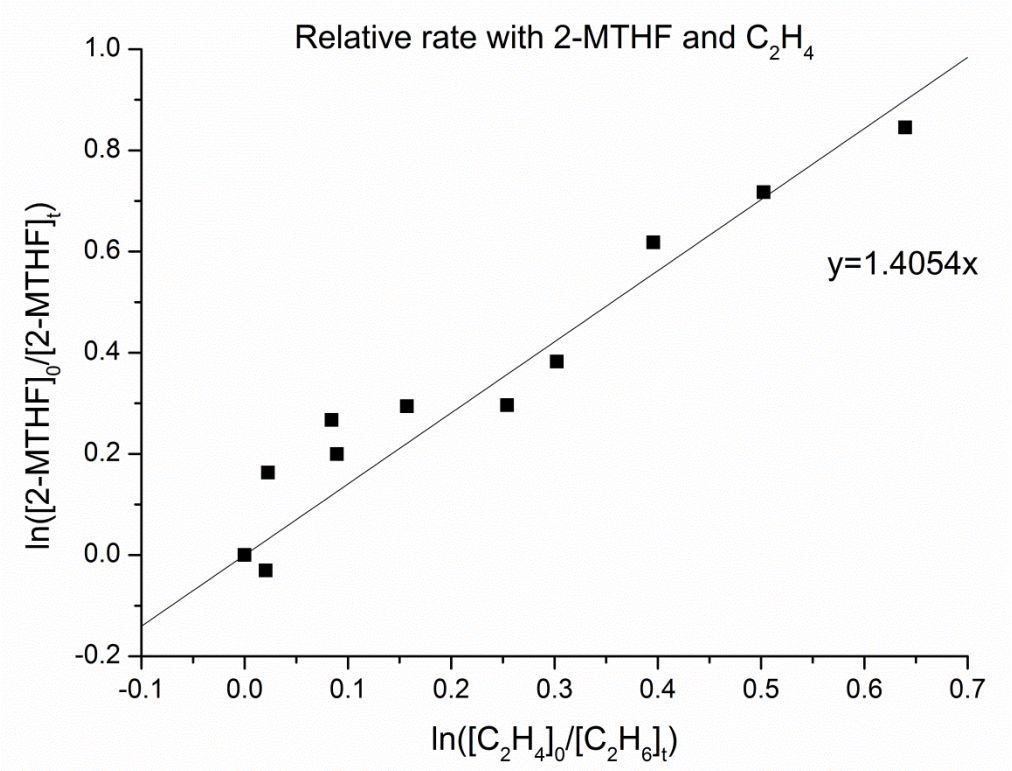


Figure 15. The data points and linear regression for the experiment with 2-MTHF and C_2H_4 reactions.

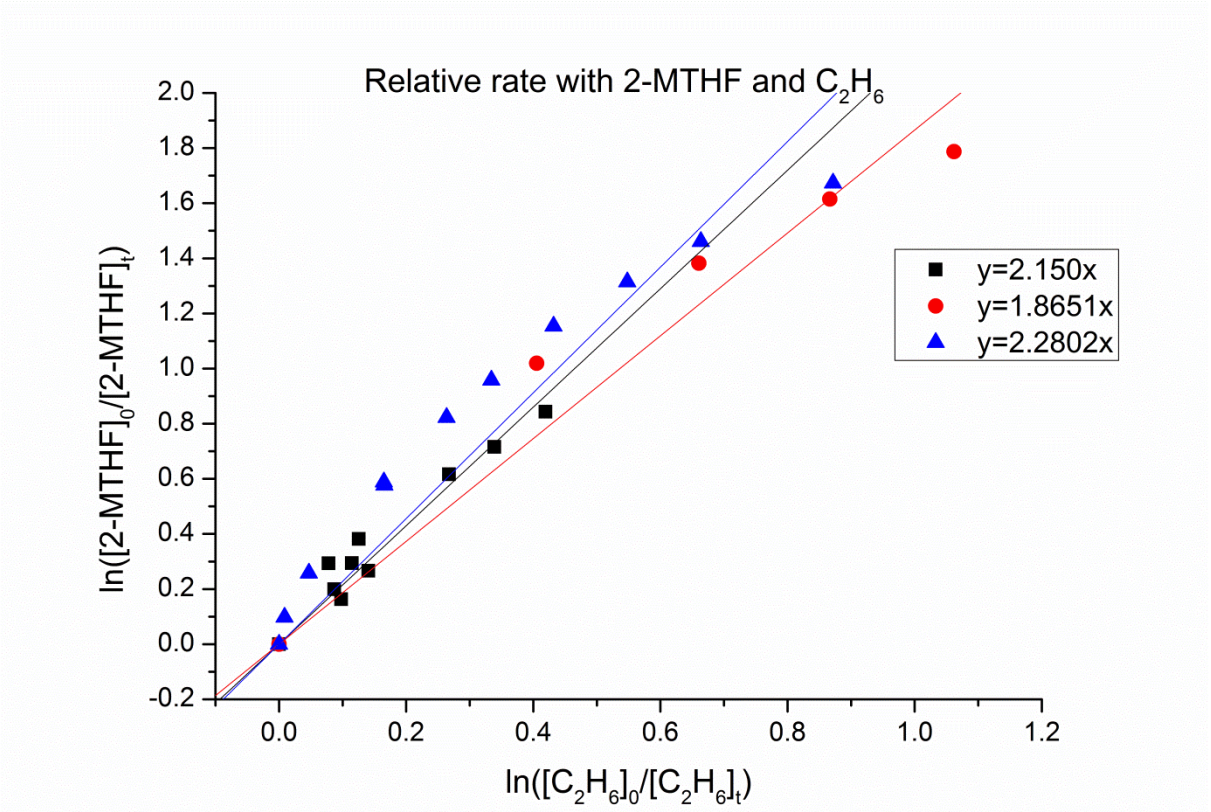


Figure 16. The data points and linear regressions for three experiments with 2-MTHF and C_2H_6 reactions.

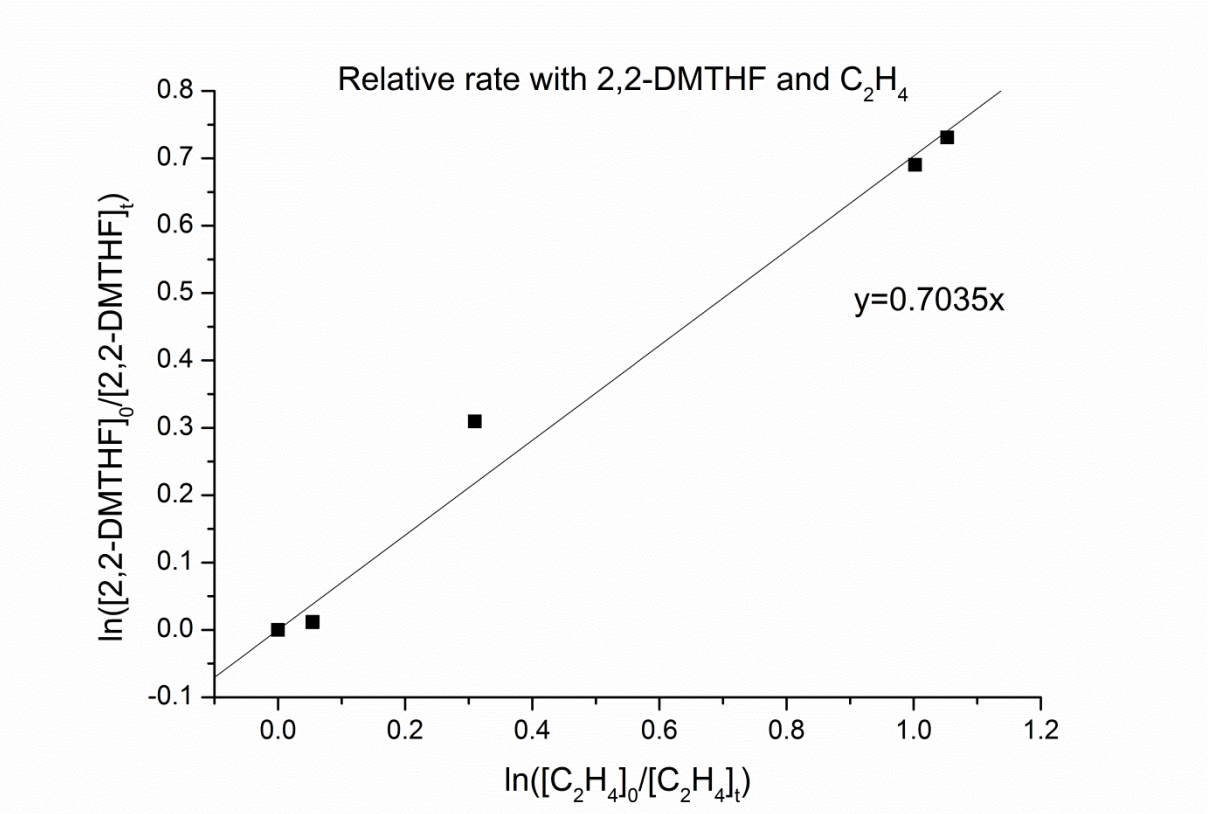


Figure 17. The data points and linear regression for the experiment with 2,2-DMTHF and C_2H_4 reactions.

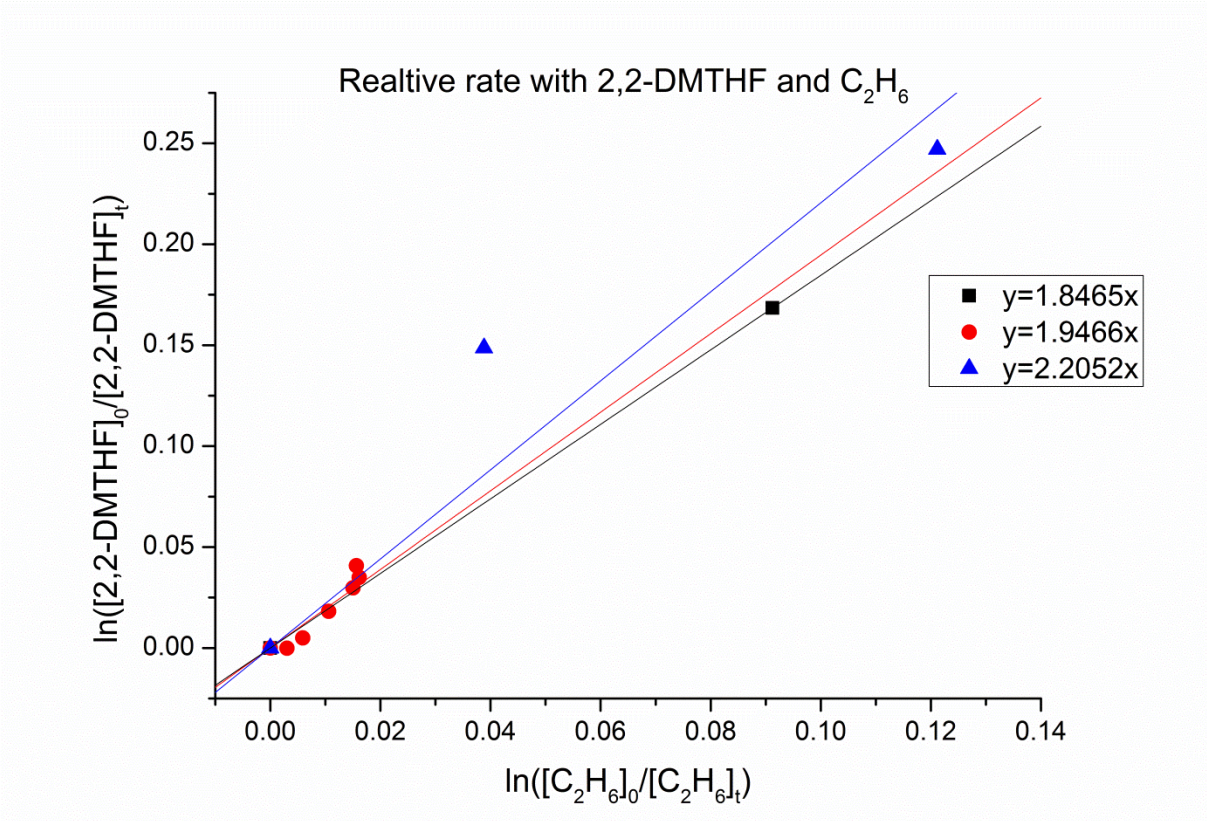


Figure 18. The data points and linear regressions for three experiments with 2,2-DMTHF and C_2H_6 reactions.

The data from Figure 15-18 are summarized in Table 7 were the calculated values for the rate coefficients are presented.

Furan	**Reference**	k_f/k_r	k_r/ $\mathbf{cm^3 molecule^{-1} s^{-1}}$	k_f/ $\mathbf{10^{-10} cm^3 molecule^{-1} s^{-1}}$
2-MTHF	C_2H_4	1.4054	$9.29 \cdot 10^{-11}$	1.3842
2-MTHF	C_2H_6	2.150	$5.70 \cdot 10^{-11}$	1.2255
2-MTHF	C_2H_6	1.8651	$5.70 \cdot 10^{-11}$	1.0631
2-MTHF	C_2H_6	2.2802	$5.70 \cdot 10^{-11}$	1.2997
2,2-DMTHF	C_2H_4	0.7035	$9.29 \cdot 10^{-11}$	0.6536
2,2-DMTHF	C_2H_6	1.8465	$5.70 \cdot 10^{-11}$	1.0525
2,2-DMTHF	C_2H_6	1.9466	$5.70 \cdot 10^{-11}$	1.1096
2,2-DMTHF	C_2H_6	2.2052	$5.70 \cdot 10^{-11}$	1.2570

Table 7. Summary of the results from the relative rate experiments for 2-MTHF and 2,2-DMTHF.

4.3 Product studies

The product studies resulted in the spectra shown in Figure 19-20 and 22-23. Each figure represents the final spectrum from the photolysis series and thus contains as much and many of the products as possible.

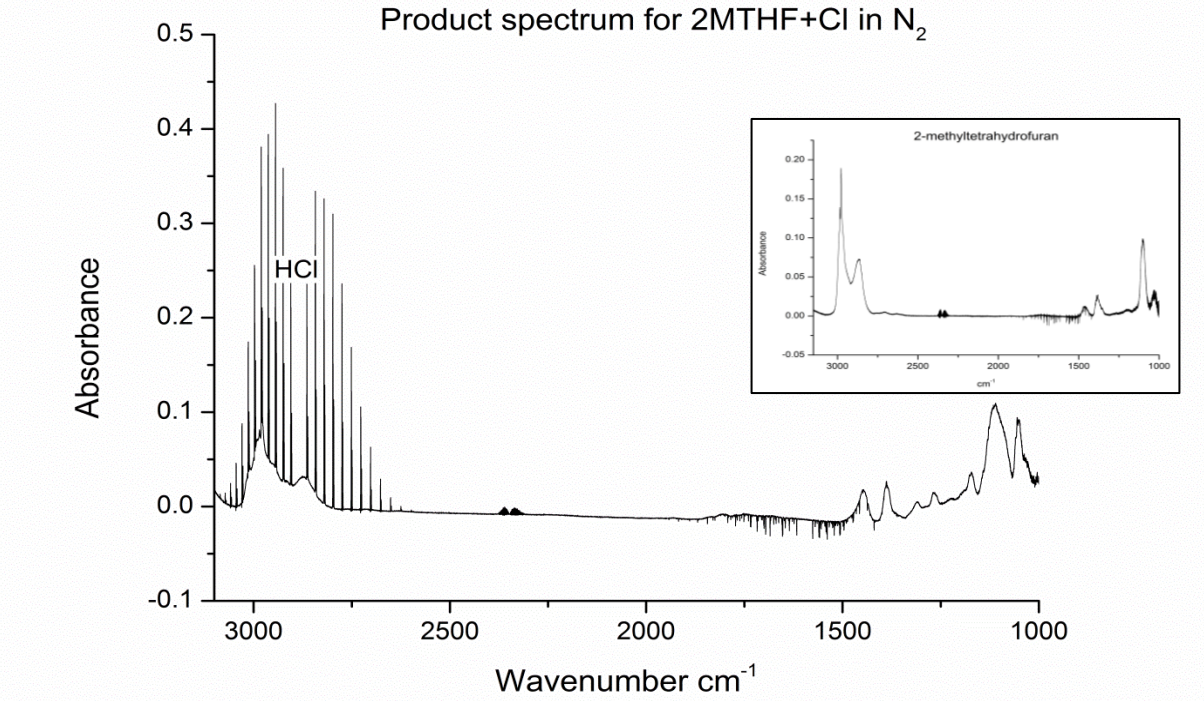


Figure 19. Product study of 2-MTHF in an environment with only N_2 as background gas. The inserted picture is Figure 8, the spectrum of 2-MTHF.

The main visible product in Figure 17 is HCl between approximately 2500 cm^{-1} and 3000 cm^{-1}. It is also seen that some extra structure is building up in the region 1000-1500 cm^{-1} comparing to the structure of 2-MTHF.

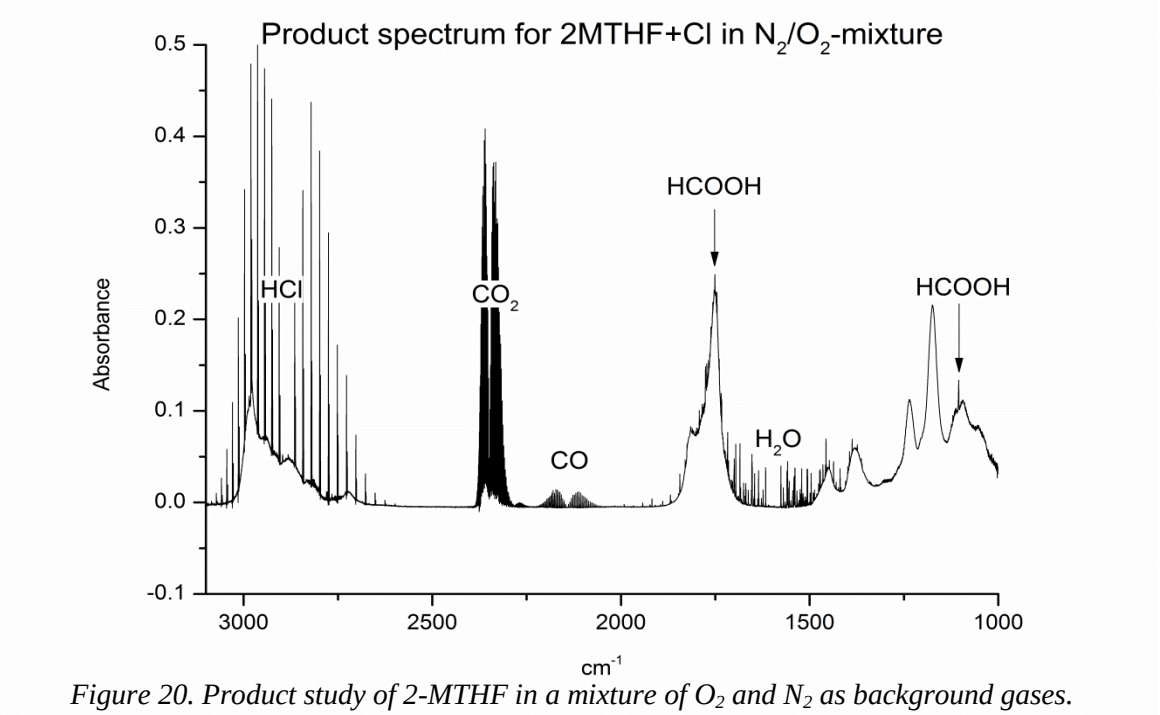


Figure 20. Product study of 2-MTHF in a mixture of O_2 and N_2 as background gases.

Some differences between reactions with and without O_2 are clearly visible. Primarily the concentrations of CO_2, CO and H_2O are much higher and the HCl is not as dominant as in Figure 19. There is also a strong peak around 1800 cm^{-1} which, if comparing with Table 1 in section 2.5.2, belongs to carbonyl groups. There are structures from many carbonyl peaks present and one of them was identified as formic acid, HCOOH. This is not at all present in the study with only N_2. The spectrum of formic acid in this region is shown in Figure 21.

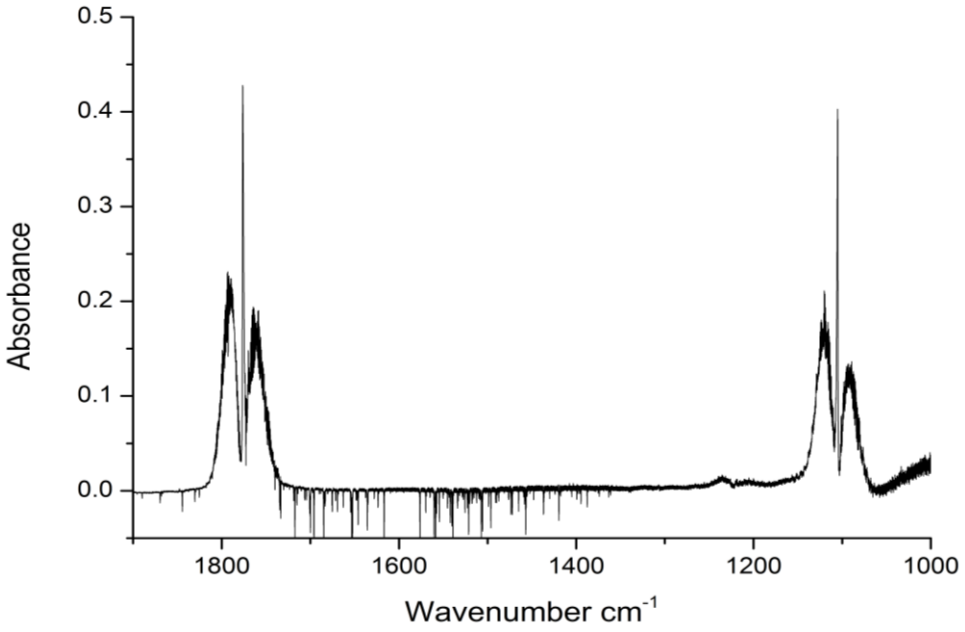


Figure 21. The infrared spectrum of formic acid, HCOOH, in the region 1000-1900 cm^{-1}, where many of the products from the furan reactions can be found.

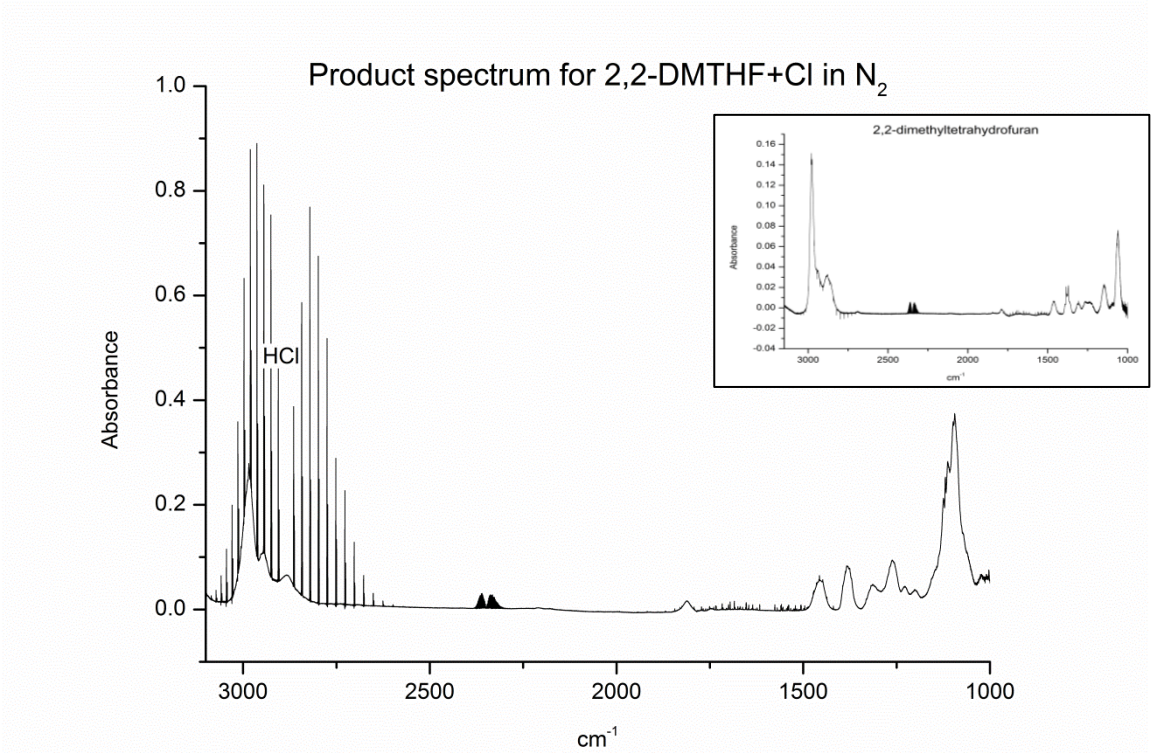


Figure 22. Product study of 2,2-DMTHF in an environment with only N_2 as background gas. The inserted picture is Figure 9, the spectrum of 2,2-DMTHF.

Similarly to the 2-MTHF, the major product for the reaction between 2,2-DMTHF and Cl in the absence of O_2 is HCl. When O_2 is present, as in Figure 23 below, there is also a similar result with a lot of CO_2, CO, H_2O and COOH. The other products seen in the spectra, can not be determined at the moment for neither of the furans.

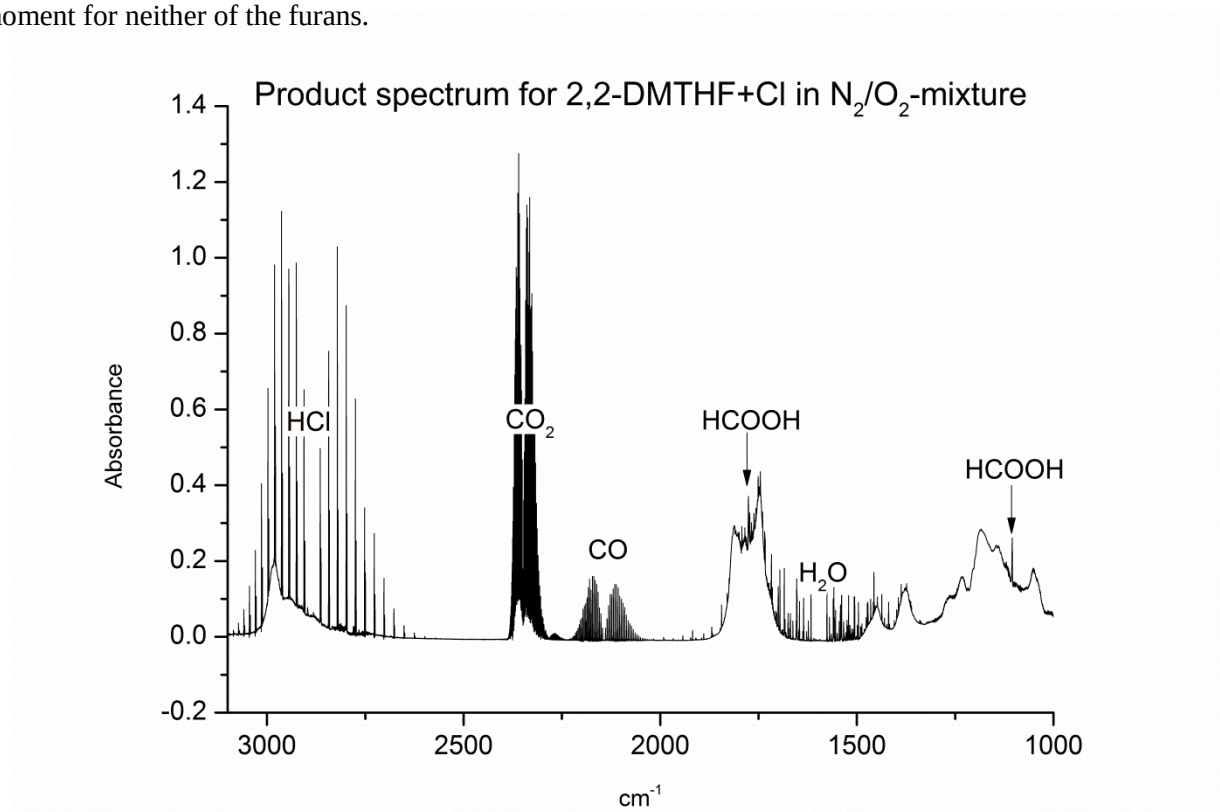


Figure 23. Product study of 2,2-DMTHF in an environment with a mixture of O_2 and N_2 as background gases.

5. Discussion

To be able to state a value of the rate coefficient for a reaction between two compounds, there must be data with high enough quality available. In this experimental work, a lot of effort has been put into executing the experiments as carefully as possible. The details of the work have continuously been written down and the cleaning, or vacuum pumping, done carefully to remove air and other remainders between the events.

Some factors are not that easy to control, e.g. the mirrors in the reaction chamber might move a little bit due to the large pressure changes, when the chamber is filled from almost vacuum up to atmospheric pressure several times a day. This might result in a reduced signal from the detector, but didn't cause any problems. Since there is a five minute pause between inserting the compounds and recording the spectrum of the sample, problems with incomplete mixing of the gases and wall reactions are significantly reduced.

Comparing Figure 8 and 9 it is clear that the 2-MTHF and the 2,2-DMTHF have very similar infrared spectra. Since these two molecules have a very similar structure they will also show similar behavior in many aspects. The shape of the spectra comes from the same type of molecular vibrations as e.g. the C-H stretch around 3000 cm^{-1}. The extra methyl group of 2,2-DMTHF results in a little bit more structure in the spectrum and the shape is not always so smooth.

It required some work to find the optimal amount of 2-MTHF and 2,2-DMTHF to use in the experiments. It is good to have relatively high and distinct absorption peaks, partly for a clearer visual spectrum to look at and partly for an easier analysis for the program. It is however important not to have too high concentrations. If the absorption peaks are saturated i.e. have an absorbance close to 1, the detector does no longer show a linear relationship and the concentrations calculated by the program can be wrong. Thus efforts were made to achieve an amplitude of 0.1-0.6 on the absorbance scale for each experiment. Some problems arose in the relative rate experiments when trying to get good amplitudes for both the furan and the reference at the same time. The ratio concluded successful was approximately 7:10, i.e. a little bit more reference than furan. In the product studies the problem with saturation regarded the absorption peaks of the products instead. Using too much of the reactants resulted in very high amounts of products, mainly HCl and CO_2, so one must take this into account when analyzing as well.

Even though good gas mixtures were achieved the greatest problem was definitely the photolysis time. The fact that the lamps and the time they are shining is controlled manually makes the uncertainties larger and the results less useful. Since both the furans react very quickly, many of the final photolysis steps were sort of unnecessary because they start to differ from the straight line in the relative rate plots more and more. Since the photolysis time in principle became based on the reaction time of the laboratory assistants, this was a major disadvantage of the experimental set up.

For the relative rate experiments it would be optimal to analyze the furan and the reference in an area where no products are building up. This can disturb the analysis in that region. This resulted in that in most of the cases C_2H_6 concentrations were calculated using an area with a range of about 10 cm^{-1}. This is not perfect since there was no base line to use, i.e. a region with no absorption peaks that can be considered as a zero level. But since the spectra looked reasonable and it is the relative concentrations that are of interest, this might not have disturbed so much. However if all the products from the reaction are identified, these can be included in the analysis and there would be no reason to avoid them.

The plan was to have at least two relative rate experiments with each combination of furan and reference, e.g. two identical experiments with 2-MTHF and C_2H_4 etc., to be able to see if the results were reliable. If the values would differ extremely, then it would not be possible to say if the rate constants were reasonable or not. Since not all experiments resulted in good analyses and could not be used as results, the new, updated goal became to have at least three satisfying experiments, one with one of the references, and two with the other. This was achieved and after improved analyses with C_2H_6 there was one good analysis with C_2H_4 and three good with C_2H_6 for each furan. The results differ quite a lot and a precise value for the rate constants cannot be stated. The mean values are roughly $k_{2\text{-}MTHF+Cl} = 1.3 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$ and $k_{2,2\text{-}DMTHF+Cl} = 1 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$. Since the analysis of C_2H_6 has been questioned it is not impossible that some values are incorrect due to poor analysis of the program, but this cannot be concluded until more data is available. It is however good that the rate constant is approximately the same in both the experiments with C_2H_4 and with C_2H_6 with 2-MTHF. For 2,2-DMTHF, there is one value ($k_{2,2\text{-}DMTHF+Cl} = 0.6536 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$) that differs from the others. The problematic thing is that it is the only experiment with C_2H_4 as a reference compound. The other three values are not that consistent either. The uncertainty is thus larger for the rate constant of 2,2-DMTHF than of 2-MTHF at the moment. The values, even if roughly determined, can be compared with the only existing rate constant, namely for the reaction between 2-MTHF and OH, which is $k_{2\text{-}MTHF+OH} = (2.53 \pm 0.31) \cdot 10^{-11}$ $cm^3molecule^{-1}s^{-1}$ [11]. It is seen that the reaction with Cl has a rate constant that is about one order of magnitude larger than for OH.

There are other previous studies that can be interesting to compare with. This includes reaction rates for furan and THF, which do not have additional methyl groups. The rate coefficients available in the literature are $k_{furan+Cl} = 2.0 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$ [10], $k_{furan+OH} = 4.19 \cdot 10^{-11}$ $cm^3molecule^{-1}s^{-1}$ [21] and $k_{THF+OH} = 1.61 \cdot 10^{-11}$ $cm^3molecule^{-1}s^{-1}$ [22]. The coefficient for the chlorine reaction with furan is in the same order of magnitude as the ones for 2-MTHF and 2,2-DMTHF determined in this project. Even though the reaction rates are similar for the furan and 2-MTHF and 2,2-DMTHF the reaction mechanisms may be different. There is no product study to compare with but since the furan contains double bonds and the others do not, it is plausible that the reactions with between Cl and furan will be addition reactions while the reactions studied in this work are abstraction reactions. To see how the chemical structure affects the reaction rate, the coefficients for OH reactions can be ordered as

$$k_{furan+OH} > k_{2\text{-}MTHF+OH} > k_{THF+OH}$$

where it seems like the additional methyl group for the 2-MTHF increases the reaction speed. From the data of this work it seems like it is the opposite since

$$k_{2\text{-}MTHF+Cl} > k_{2,2\text{-}DMTHF+Cl}.$$

If this this suggests that the result from this study, or the previous, perhaps is wrong, or if it is simply shows that there is a difference between OH and Cl reactions cannot be determined today. To see how the Cl and OH reaction differ, all the products and the reaction mechanics must be known better. It should be remembered that all three tetrahydrofurans are not present in these comparisons; it might be so that the speed of the reaction is not proportionally connected to the number of methyl groups. There is a theoretical study that supports the results from this project [23]. The conclusions in this work are that hydrogen abstraction is most likely to occur at coal atom number 2 (see section 1.3.1) and then coal atom number five is preferred to number three and four and also to the methyl group. Since there is no hydrogen atom present at coal atom number two in 2,2-DMTHF (all bonds are between coal atoms in the ring ant the methyl groups) there cannot be any hydrogen abstraction at this place. So the next preferable hydrogen atom, i.e. at number 5, is abstracted but this reaction is slower. So altogether

the $k_{2,2\text{-}DMTHF}$ should be smaller than $k_{2\text{-}MTHF}$ for any hydrogen abstraction reaction according to the theoretical study.

From the product studies it is clearly visible that HCl is one major product, and it is most likely a result of hydrogen abstraction from the furan molecules as in reaction (2.26). For both of the furans there are clear products in the region 1000-1500 cm^{-1} and around 3000 cm^{-1}, i.e. in the regions where the furans themselves have their characteristic features. This might indicate that the products have a similar chemical structure as the furans, and perhaps some ring shaped molecules can be found with further investigations. This is not unlikely since the reactions can take place at the methyl group, and would thus result in that the rings are not opened and reformed into other molecules during the reactions. In the product studies where O_2 was present there were clearly more CO_2, CO and H_2O which is logical since these contain oxygen. It is also in common for the two furans that there is a strong and broad product peak around 1750 cm^{-1} indicating a carbonyl bond (see Table 1), which is not at all visible in the reactions with only N_2. In the experiments where O_2 was absent it seems to be more HCl formed, which might be due to that there are not as many reaction possibilities when O_2 is not present, but hydrogen abstraction will be dominant. For the moment the products mentioned above are the only ones that can be determined quantitatively; this is because it does not exist reference spectra for all the chlorinated products formed, especially not ring shaped products since these have not been investigated to any large extent.

The product spectra have been compared with the spectra of some plausible products in these types of reactions. This is done through comparing magnitude and position of peaks in existing spectra. It has been concluded that there is no sight of ethane, acetone, propene, acetaldehyde, formaldehyde, ethyl-vinyl ether, 1- or 2- butene. Characteristic peaks of some acids have been seen and specifically formic acid. For the other products, it is harder to identify specific molecules because they are larger. Then there are more opportunities with small differences in chemical structure to choose from, and the differences in the spectra are small. Thus it can be concluded that some acids are formed, but not exactly which.

6. Conclusions and future work

For continued experiments and research with reactions that happens so quick as the furan-chlorine reactions, some kind of device or program where the photolysis time can be determined with an accuracy of perhaps 0.2 s would be a great advantage.

With the experience from the analysis in this project, some conclusions and recommendations for future studies can be mentioned. The conclusion can be drawn that as long as the products are unknown, it is desirable to analyze the furan and the reference in an area where no products are building up. Both 2-MTHF and 2,2-DMTHF have two regions where there are distinct peaks, and the region with the higher wavenumber, i.e. 2700-3070 cm^{-1}, is the best to use for both of them. This is because of the products that become present in the lower wavenumber region. The phenomenon with a strange curve beyond approximately 3070 cm^{-1} in the spectra, see e.g. in Figure 8 and 9, is due to ice in the detector. It is important not to analyze in this region since the shape changes from time to time. If there is need for using this region it is possible to clean the detector, but since our spectra was analyzed for wave number lower than 3070 cm^{-1} this was not necessary.

The reference spectra for C_2H_4 was ok to use from the *HITRAN* database and the best analysis region was again 2700-3070 cm^{-1} and it was many times possible to analyze the furan and C_2H_4 at the same time. If it is not working to analyze two compounds at the same time, it is possible to do as for C_2H_6. The reference spectrum from the *HITRAN* database was not good enough for C_2H_6. It is thus necessary to use a measured one to get any results. It might also be necessary to use a small analysis interval between two HCl peaks, as a suggestion 2999-3009 cm^{-1} worked quite well. If the analysis does not work the first time, the intervals can of course be changed a little bit. If there is no region where the analysis is good, e.g. no decrease with time can be seen, then the experiment should be redone and perhaps with a higher concentration to get a more intense absorption spectrum.

It could be worth considering using another reference compound than C_2H_6 since its most useful absorption peak almost completely overlaps with the furans. A reference that has some peaks in an area where no furan, and no products, is present would also be an advantage.

If these improvements are made it would be good to repeat the experiments at least once to complement the results from this work. The values for the rate constants have a quite high uncertainty for the moment and continued work is needed to fully confirm the reaction speed of these reactions.

For the data available now the reaction rates can be ordered as follows,

$$k_{2\text{-MTHF+Cl}} > k_{2,2\text{-DMTHF+Cl}} > k_{2\text{-MTHF+OH}}$$

and the total reaction rate for each of these reactions is dependent on the abundance of OH and Cl respectively. But it can be concluded that in areas with a higher level of Cl in the air, the reactions concerned in this work are an important reaction pathway for 2-MTHF and 2,2-DMTHF.

The so far unknown products must be investigated more and perhaps with other methods, like mass spectroscopy, as well. When all the products are determined it is possible to quantify them. Then a mass balance for carbon atoms, i.e. the number of atoms before and the number after the reaction, can be set up and tell more about the reaction path ways.

6.1 Answer to Questions

1a. What are the reactions rate coefficients for the two compounds 2-MTHF and 2,2-DMTHF against reactions with and Cl-atoms?

For reactions with Cl the rates are roughly: $k_{2\text{-}MTHF+Cl} = 1.3 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$ and $k_{2,2\text{-}DMTHF+Cl} = 1 \cdot 10^{-10}$ $cm^3molecule^{-1}s^{-1}$.

1b. How do these values compare with previous results for reactions with OH.

The rate coefficients for the reactions between 2-MTHF and Cl, and 2,2-DMTHF and Cl, are both higher than for the known coefficient for 2-MTHF, which is the only investigated tetrahydrofuran with an extra methyl group.

2a. What are the identifiable products from these reactions?

The known products that will form in these reactions in the atmosphere are HCl, CO_2, CO, H_2O and HCOOH.

2b. How do the products from the Cl reactions differ depending on whether there is oxygen present or not? I.e. if the reaction takes place in N_2 or in an O_2/N_2 mixture.

In the atmosphere, where O_2 is always present, all the products mentioned in question 2a will be formed. In the reactions where O_2 was absent there were simply not any products containing oxygen, but primarily HCl. This indicates that the ring structure of the molecule is intact.

3. How does the number of additional methyl groups affect the properties of the tetrahydrofurans?

No absolute conclusion can be drawn here, but it seems like additional methyl groups slows down the reaction with Cl. They are however in the same order of magnitude and do not differ extremely.

4. How do these two compounds differ from those without methyl groups (furan and THF), including both the reaction rate constants and the product distribution?

The conclusion about the reaction rate is the same as in question 3, i.e. additional methyl groups might slow down the reaction. The difference between furan and tetrahydrofurans in general is the reaction mechanism, i.e. that addition reactions for furan since it contains double bonds and abstraction reactions for the tetrahydrofurans

5a. What can be concluded about the environmental impact, e.g. air quality, of these compounds on a local and a global scale?

One thing that can be concluded about the atmospheric impact of the furans is that due to their high reaction rates, 2-MTHF and 2,2-DMTHF will have short lifetimes against Cl in the atmosphere. Since the reactions with OH also will take place, and probably at a similarly high speed since it is more abundant in the air, this means that the furans will not have time to reach the stratosphere. This is an important conclusion since it will only affect the tropospheric chemistry and not the stratospheric.

5b. What is the GWP of the furans?

To be able to determine the GWP of 2-MTHF and 2,2-DMTHF, and make a decision whether these are qualified candidates as biofuels, corresponding experiments with OH must be performed. When the rate coefficients for reactions with OH are known the GWP can be estimated.

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