Atmospheric Chemistry and Climate Coupling:
Reaction Kinetics and Photochemical Study of Selected
Fluorinated and Oxygen Containing Organic Molecules

Summary of PhD Thesis

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1. Introduction

Focus of recent atmospheric chemistry research is the basic question of how Global warming affects the chemistry of the atmosphere, and how the composition change caused by atmospheric reactions feedbacks to climate change. It is relatively little known that climate forcing of the chemically active greenhouse gases (GHGs) is approximately half of that of the most important GHG, carbon dioxide. In my PhD thesis I have dealt with such elementary chemical reactions and photochemical processes that are related to the atmospheric chemistry of a novel air conditioning agent, HFC-161 (C_2H_5F) and also to those that participate in the formation of one of the most important greenhouse gases, the tropospheric ozone, which, in addition, is also an important air pollutant.

The atmospheric photo-oxidation of C_2H_5F is initiated by the reaction with OH radicals, and acetyl fluoride (CH_3C(O)F) is formed as a reaction intermediate during its subsequent depletion processes. A central subject of my PhD thesis is the study of the reaction kinetics and photochemistry of acetyl fluoride about which no information is available from previous works. The investigation of acetyl fluoride is interesting and important not only for atmospheric chemistry reasons, but also because it makes possible the study of the effect of F-substitution on kinetics, spectroscopic and photochemical properties. The elementary reactions of carbonyl molecules and carbonyl free radicals are very important in the formation of O_3 in the troposphere. Such reactions have also been subjects of my PhD thesis.

I have applied the “fundamental approach” in my research: I wished to get new knowledge about the reaction kinetics, photochemistry, and molecular mechanisms of the studied processes. Beside this basic concept, the reaction kinetic and photochemical parameters determined are expected to be utilised in atmospheric chemistry models, which are used, for example, to predict smog episodes in the polluted urban air.

I have performed laboratory investigations of the following processes:

\[
\begin{align*}
\text{OH} + \text{C}_2\text{H}_5\text{F} & \rightarrow \text{products} \quad (1) \quad k_1 \\
\text{OH} + \text{CH}_3\text{C}(\text{O})\text{F} & \rightarrow \text{products} \quad (2) \quad k_2(T) \\
\text{CH}_3\text{C}(\text{O})\text{F} + \text{hv} & \rightarrow \text{products} \quad (3) \quad \Phi_3, \sigma_{\text{AcF}}(\lambda) \\
\text{CH}_3\text{C}(\text{O})\text{F} + \text{hv} & \rightarrow \text{CH}_3 + \text{FCO} \quad (3a) \\
\text{CH}_3\text{C}(\text{O})\text{F} + \text{hv} & \rightarrow \text{CH}_3\text{F} + \text{CO} \quad (3b) \\
\text{OH} + \text{CF}_2\text{COOH} & \rightarrow \text{products} \quad (4) \quad k_4 \\
\text{C}_2\text{H}_5\text{CO} + \text{O}_2 & \rightarrow \text{products} \quad (5) \\
\text{C}_2\text{H}_5\text{CO} + \text{O}_2 + \text{M} & \rightarrow \text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{M} \quad (5a) \\
\text{C}_2\text{H}_5\text{CO} + \text{O}_2 & \rightarrow \text{OH} + \text{products} \quad (5b) \quad \Gamma_{5b} = k_{5b}/k_5 \\
(\text{CH}_3)_3\text{COCO} + \text{O}_2 & \rightarrow \text{products} \quad (6) \\
(\text{CH}_3)_3\text{COCO} + \text{O}_2 + \text{M} & \rightarrow (\text{CH}_3)_3\text{C}(\text{O})\text{O}_2 \quad (6a) \\
(\text{CH}_3)_3\text{COCO} + \text{O}_2 & \rightarrow \text{OH} + \text{products} \quad (6b) \quad \Gamma_{6b} = k_{6b}/k_6 \\
\text{CH}_3\text{COCH}_2 + \text{Br}_2 & \rightarrow \text{products} \quad (7) \quad k_7(T) \\
\text{OH} + \text{C}_2\text{H}_5\text{CHO} & \rightarrow \text{C}_2\text{H}_5\text{CO} + \text{H}_2\text{O} \quad (8) \quad k_8 \\
\text{OH} + (\text{CH}_3)_2\text{CC}(\text{O})\text{H} & \rightarrow (\text{CH}_3)_2\text{CC}(\text{O}) + \text{H}_2\text{O} \quad (9) \quad k_9 \\
\text{Br} + \text{C}_2\text{H}_6 & \rightarrow \text{products} \quad (10) \quad k_{10} \\
\text{Br} + \text{CH}_2\text{ClBr} & \rightarrow \text{products} \quad (11) \\
\text{Br} + \text{neo-C}_2\text{H}_12 & \rightarrow \text{products} \quad (12)
\end{align*}
\]

I have determined rate coefficients \((k_1, k_2(T), k_4, k_7(T), k_8, k_{10})\), absorption cross section \((\sigma_{\text{AcF}}(\lambda))\), photodissociation quantum yield \((\Phi_3)\) and OH branching ratios \((\Gamma_{5b} = k_{5b}/k_5\) and \(\Gamma_{6b} = k_{6b}/k_6\)). The kinetic and photochemical parameters determined allow predictions to be made on the relationship between molecular structure and reactivity as well as the estimation of atmospheric lifetimes of a few organic molecules.
2. Experimental

In my research I have studied a variety of elementary chemical reactions and photochemical processes. Thus, in order to get reliable results, I have applied several techniques and methods to carry out the experiments.

The majority of the investigations were performed by using the so called "direct" or "absolute" reaction kinetic methods. A common feature of them is that the reacting atoms, or free radicals are monitored directly, usually using different optical methods, and the observation is made on the millisecond or microsecond timescale of the elementary reactions. Both the complementary direct techniques of pulsed laser photolysis (PLP) and fast discharge flow (DF) have been used. The PLP apparatus and experimental procedure have been developed for its most part in my present PhD work. The OH radicals were generated by the 248 nm exciplex laser photolysis of nitric acid (HNO$_3$) and its detection was achieved by using resonance fluorescence (RF). The analytical light source was an OH resonance fluorescence lamp operated by a microwave generator discharging water vapour in He flow (both the excitation and the detection were at 308 nm). The rate coefficient of the studied reaction was determined by monitoring and analyzing the depletion of the OH-RF signals at the laboratory time scale. The experiments were controlled and the data analyzed by a LabView-based hardware-software system.

In the case of the DF technique, the reactions were carried out in a tube reactor, in high velocity helium carrier gas. The free radicals were produced by microwave discharge and fast thermal reactions inside the moveable injector attached coaxially to the reactor. The reaction time was set by the distance between the end of the injector and the detection cell as well as the linear flow rate. The reaction time was varied by varying the position of the moveable injector. In the DF experiments, the RF detection was also used, but the acetyl radical (CH$_3$C(O)CH$_2$) was monitored by laser induced fluorescence (LIF). The excitation light was providing by a Nd:YAG laser at 355 nm and the detection was done at 436 nm. The magnitude of the RF and LIF signals were proportional to the concentration of the transients, which were recorder at different reaction distances. The direct kinetic measurements were performed in high excess of the reactants over the free radicals, that is, under pseudo first order conditions.

Beside the direct kinetic experiments, relative rate (RR) kinetic measurements were also carried out. In this case, the rate of the studied reaction has been compared with that of a reference reaction the rate coefficient of which is well known. Rate coefficient ratios were determined in the experiments which were resolved to absolute $k$-values by making use of the rate coefficient of the reference reaction. The RR experiments were carried out in a "smog chamber" type apparatus, the photolysis light source was a high-power xenon lamp.

The photochemical studies were performed using pulsed laser photolysis. In order to determine the photodissociation quantum yield, the absorption cross section of the photolyte molecule is needed. The absorption cross section as a function of wavelength was usually determined by applying a home constructed gas spectrophotometer operated under flow trough conditions. For the determination of the photo dissociation quantum yield, the depletion of the photolyte was measured with gas chromatographic (GC) analyses. The photolyses were done by using an exciplex laser at 248 nm wavelength. At regular time intervals, samples from the photolysed mixture were withdrawn by using a micro-syringe, and the number of laser pulses (photolysis time), as well as the laser energy per pulse were measured. The photo dissociation quantum yield was obtained by the measured concentration depletion, the absorbed energy and the absorption cross section.
3. Results

3.1 Photochemical and Reaction Kinetic Study of Freon Replacements and their Atmospheric Degradation Intermediates

3.1.1 The Reactions of OH Radicals with C$_2$H$_5$F (HFC-161) and CH$_3$C(O)F

Objectives of the kinetic study of the reaction of OH with ethyl-fluoride were to test the newly installed PLP-RF apparatus and procedure, as well as to provide kinetic result by the application of the DF-RF method the first time. In both cases, the experiments were conducted at room temperature and $p \approx 100$ mbar and $p \approx 3$ mbar pressures in the PLP and DF kinetic experiments, respectively (helium was the buffer gas). Representative experimental results from PLP-RF experiments are shown in Fig. 1. Under pseudo first order conditions, at the low OH concentration ([C$_3$H$_2$C(O)F] >> [OH]$_0 \approx 10^{12}$ molecule cm$^{-3}$), the reaction obeyed first order kinetics, as it is seen by the measured OH depletion curves presented in Fig. 1. The rate coefficient determined from the PLP-RF study is $k_1$ (300 K) = (2.35 ± 0.07) $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

In the DF-RF experiments, the OH radicals were produced by reacting H atoms with NO$_2$, while the H atoms were obtained by discharging molecular hydrogen in He flow. The experiments were carried out in a great excess of ethyl-fluoride over OH ([OH]$_0 \approx 4 \times 10^{11}$ molecule cm$^{-3}$). The so called “on-off” technique was applied, that is, the OH signal strength was recorded, as a function of the varied reaction distance, in the presence and absence of ethyl-fluoride, respectively. Using this “on-off” technique one automatically corrects for the wall consumption of the OH radical. Such experimental procedure was used also in the study of the OH + acetyl-fluoride reaction (see below). Since the inner surface of the flow tube was coated with an inert cover, the heterogeneous loss of OH was only of minor significance.

The rate coefficient of $k_1$ (297 K) = (1.90 ± 0.19) $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ has been determined by the DF-RF experiments. The good agreement of the two values justifies their averaging, and so the rate coefficient of $k_1$ (298 K) = (2.13 ± 0.19) $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is proposed for the OH + ethyl-fluoride reaction. This value agrees very well with the recommendation of the critical kinetic data evaluations. It is important to note, moreover, that
the rate coefficient for the OH + C₂H₅F (1) has not been determined previously by using a thermal reaction kinetic method, such as DF.

Acetyl-fluoride is formed in the photo-oxidation of ethyl-fluoride in the atmosphere as it has has been confirmed by smog-chamber experiments in the current PhD work. The reaction of acetyl-fluoride with OH radicals has not been studied previously, contrary that this reaction is of importance from both fundamental chemical kinetics and practical atmospheric chemistry reasons alike. The rate coefficient of the reaction has been determined in the temperature range of $T = 300–410 \text{ K}$ by applying the DF-RF method. A typical experimental result is presented in Fig. 2.

![Figure 2](image)

**Figure 2.** Representative experimental results obtained from DF-RF experiments for the reaction OH + CH₃C(O)F (2). Insert: selected OH depletions in semi-logarithmic plot, $S_{\text{on}}^{\text{OH}}$ and $S_{\text{off}}^{\text{OH}}$ designate the OH signal magnitude in the presence and absence of acetyl-fluoride, respectively (“on-off technique”), and $\Delta z$ is the varied reaction distance. The slopes of the straight lines are proportional $k_2'$, the pseudo first order rate coefficient. The main panel of the figure shows the $k_2' - [\text{CH}_3\text{C(O)F}]$ plot, the slope of the straight line provides the rate coefficient of the overall reaction, $k_2(342 \text{ K})$.

The rate coefficient determined at laboratory temperature is $k_2(300 \text{ K}) = (0.74 \pm 0.05) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is much smaller than the rate coefficients of most of the OH-reactions, e. g., that of the OH + acetone reaction (Fig. 3). This observation is understood by the strong negative inductive effect of the fluorine substituent and the known electrophilic property of the OH radical. The group reactivity value of $F(\text{FCO}) = 0.054$ ($T = 300 \text{ K}$) is proposed by the measured rate coefficient, which can be utilized for the estimation of the rate coefficient of other OH + acyl-fluoride reactions. The temperature dependence of the rate coefficient of the OH + CH₃C(O)F (2) reaction is presented in Fig. 3 in Arrhenius representation, that is, the logarithm of the rate coefficient is plotted against the reciprocal of the absolute reaction temperature. As seen, the reaction does not follow the Arrhenius law, that would provide a straight line, but, instead, the Arrhenius plot is “curved”: in the lower temperature region, the rate coefficient decreases only slightly with decreasing temperature. The observed temperature dependence is well described by the expression $k_2 = 3.6 \times 10^{-3} \exp(-1.05 \times 10^{-2}/T) + 1.56 \times 10^{-13} \exp(-9.1 \times 10^{-4}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The deviation from the Arrhenius law is probably caused by quantum chemical tunnelling effect, as it has been suggested by theoretician colleagues. It is noted that such non-Arrhenius behaviour is more common in the reactions of OH radicals with polar molecules than believed previously.
3.1.2 The Absorption Spectrum of CH$_3$C(O)F and its Photodissociation Quantum Yield

In order to determine the photo dissociation quantum yield of acetyl-fluoride, its absorption cross section ($\sigma_{AcF}$) is required at the photolysis wavelength, which was determined using a home made gas-spectrophotometer. Absorbance, $A$, was measured, the acetyl fluoride concentration was varied and by the application of the Lambert-Beer law, the absorption cross section as a function of the wavelength was constructed (Fig. 4). At 248 nm, $\sigma_{AcF}$ has also been determined by using an exciplex laser as the analytical light source with strongly reduced light intensity (Fig. 4, insert). The two methods have supplied results in good agreement, their average is $\sigma_{AcF}(248$ nm, 297 K) = $(2.03 \pm 0.04) \times 10^{-21}$ cm$^2$ molecule$^{-1}$.

The absorption spectrum of acetyl-fluoride has a wide absorption band with maximum at ~210 nm. Thus, it can be concluded that the fluorine substitution shifts the absorption spectrum strongly in the “blue” direction compared with the absorption spectra of aliphatic aldehydes, or ketones (as for instance, the maximum of the absorption spectrum of acetone is at ~280 nm). As seen in Fig. 4, my result agrees well with the only spectrum reported in the literature for CH$_3$C(O)F.
Figure 4. The absorption spectrum of acetyl fluoride. The Lambert-Beer plot in the insert shows the determination of the absorption cross section at 248 nm using a spectrophotometer and also a reduced intensity exciplex laser as analytical light source.

The photo dissociation quantum yield for acetyl-fluoride has been determined at 248 nm using exciplex laser photolysis: $\Phi_3$ (298 K, 1000 mbar air) = 0.62 ± 0.02 (Fig. 5). The ~0.7 quantum yield means the photodissociation process is dominating, but non-radiative photophysical processes may also play a roll in the mechanism. The photodissociation is lightly to occur by C–C rapture forming CH$_3$ + FCO radicals.

Figure 5. A representative plot used to determine the photodissociation quantum yield of acetyl-fluoride: [AcF]$_n$ and [AcF]$_0$ designate the measured concentration at a given reaction time and at time zero, respectively, $n$ is the number of laser pulses and $E(J)$ is the energy per pulse [3].
3.2 Oxidation Kinetics of Propionaldehyde and Pivalaldehyde

The oxidation kinetics of C\textsubscript{2}H\textsubscript{5}CHO and (CH\textsubscript{3})\textsubscript{3}CC(O)H have been studied with the DF-RF method by measuring the OH-concentration versus the reaction time in the OH + aldehyde and OH + aldehyde + O\textsubscript{2} reaction systems in back-to-back experiments. In this way, OH branching ratios (OH yields) and rate coefficients have been determined [2], [4], [6].

High OH yields have been determined for the C\textsubscript{2}H\textsubscript{5}CO + O\textsubscript{2} and (CH\textsubscript{3})\textsubscript{3}CC(O) + O\textsubscript{2} at low reaction pressures: at around 1 mbar pressure the branching ratio is close to unity, as for instance, \( \Gamma_{5b}(1.37 \text{ mbar He}) = 0.88 \pm 0.06 \). However, the OH yields have been found to decrease rapidly with the increase of pressure, e. g., at 13.34 mbar: \( \Gamma_{5b} = 0.33 \pm 0.03 \). The observed pressure dependence is understood by a „chemical activation” mechanism, in which the acyl radical combines with O\textsubscript{2} forming a vibrationally excited acyl peroxy radical. This excited radical can either be stabilized by collisions, reform the reactants, or react further to form the OH-radical product. OH radicals are known to be by far the most important reactive species in the atmosphere. Nevertheless, the strong pressure dependences observed for reactions (5b) and (6b) indicate that these reactions can not be important sources of OH radicals under atmospheric conditions.

![Figure 6. OH branching ratio for the reaction C\textsubscript{2}H\textsubscript{5}CO + O\textsubscript{2} determined in He buffer gas. The symbols designate experimental results, while the curve fitted to them is the result of theoretical computations by theoreticians cooperating on the subject [2], [6]. The insert shows OH decays in semi-logarithmic plots for the OH + C\textsubscript{2}H\textsubscript{5}CHO and OH + C\textsubscript{2}H\textsubscript{5}CHO + O\textsubscript{2} reaction systems from two representative experiments carried out back-to-back (\( p = 6.22 \text{ mbar He}, T = 300 \text{ K}, [OH]_0 \approx 2.4 \times 10^{11}, [C_2H_5CHO] = 5.35 \times 10^{12} \text{ and } [O_2] = 1.03 \times 10^{15} \text{ molecule cm}^{-3} \)).](image)

Beside OH-yields, the oxidation kinetic investigations have returned also rate coefficients for the OH + propionaldehyde (8) and OH + pivalaldehyde (9) reactions (DF-RF): \( k_8(298 \text{ K}) = (1.85 \pm 0.06) \times 10^{-11} \) and \( k_9(298 \text{ K}) = (2.65 \pm 0.17) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). They agree well with the IUPAC recommendations. [2], [4], [6]. The OH decay constants are presented in Fig. 7. in the form of the usual pseudo first order plots: the slopes provide the rate coefficients of the studied overall reactions (8) and (9).
3.3 Kinetic Study of Bromine Reactions.

A recent important development in atmospheric chemistry is the recognition that bromine reactions play an important role not only in the stratosphere, but also in the chemical processes of the troposphere. The investigations performed are related to this aspect of atmospheric chemistry.

The acetonyl (CH$_3$C(O)CH$_2$) + Br$_2$ (7) reaction has been studied using the DF-LIF method, the usual way, under pseudo first order conditions ([CH$_3$C(O)CH$_2$]$_0$ $\approx$ 4 $\times$ 10$^{11}$ molecule cm$^{-3}$). The rate coefficient of the reaction has been determined at 3 temperatures; the room temperature value is $k_7$(298 K) = (2.33 ± 0.02) 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. $k_7$ is significantly smaller than the rate coefficients of the reactions of alkyl radicals with Br$_2$. This reduced reactivity of the atmospherically important acetonyl radical is explained by its resonance stabilized molecular structure. The rate coefficient increases slightly with increasing temperature corresponding to an activation energy of $E_{A,7}$ $\approx$ 2.3 kJ mol$^{-1}$.

The rate coefficient for the reaction Br + C$_2$H$_6$ (10) has been determined by employing the relative rate kinetic method (RR); the reference reactions were Br + CH$_3$ClBr (11) and Br + neo-C$_5$H$_{12}$ (12) [1], [5]. The proposed rate coefficient is $k_{10}$ (310 K) = (3.78 ± 0.50) 10$^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This result provides the possibility of the Br + C$_2$H$_6$ reaction to be used as a reference for further RR investigations, as for instance, to study the relatively slow atmospherically important Br atom reactions. The determined $k_{10}$ rate coefficient has been used for the estimation of the standard enthalpy formation of the ethyl radical: $\Delta f^\circ_{298}(C_2H_5)$ = (122.0 ± 1.9) kJ mol$^{-1}$, which agrees very well with the generally accepted value.
4. New Scientific Results

1. The rate coefficient for the reaction of OH radicals with ethyl-fluoride has been determined by two independent experimental methods in good agreement. The proposed rate coefficient is: 
\[ k_1(298 \text{ K}) = (2.13 \pm 0.19) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \]
which is in excellent agreement with the recommendations of the critical reaction kinetics data evaluations. Acetyl-fluoride has been identified as an intermediate in the photo-oxidation of ethyl-fluoride making likely its atmospheric formation as well.

2. The first kinetic parameters have been determined for the reaction of OH radicals with acetyl-fluoride. The rate coefficient obtained at laboratory temperature, 
\[ k_2(300 \text{ K}) = (0.74 \pm 0.05) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \]
is a very small value, which can be understood, however, by structure-reactivity considerations (see point 5). Based on this rate coefficient, the 
\[ F(\text{FCO}) = 0.054 \]
group-reactivity factor is proposed that can be used for the estimation of rate coefficients for other OH + acyl-fluoride reactions. The temperature dependence of the reaction has been studied in the temperature range of \( T = 300–410 \text{ K} \). The temperature dependence of the reaction has been found to deviate of the Arrhenius-law: toward lower temperatures, the rate coefficients decreases only slightly with decreasing temperature. The temperature dependence is well described by the equation: 
\[
k_2 = 3.6 \times 10^{-3} \exp(-1.05 \times 10^{-2} / T) + 1.56 \times 10^{-13} \exp(-9.1 \times 10^{-4} / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]
The probable reason of the observed non-Arrhenius behaviour is the quantum chemical tunnelling effect that becomes important at lower temperatures.

3. The absorption spectrum of acetyl-fluoride has been found to have a wide absorption band, with maximum at \(~210 \text{ nm} \). That is, the fluorine substitution shifts the spectrum strongly to the short wavelength UV region compared, for example, with the absorption of aliphatic aldehydes and ketones. The absorption cross section at 248 nm, where the photodissociation quantum yield has been determined, is 
\[ \sigma_{\text{AcF}}(248 \text{ nm}, 297 \text{ K}) = (2.03 \pm 0.04) \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1} \]
cm\(^{-1}\). The photodissociation of acetyl-fluoride has been studied by exciplex laser photolysis; the following quantum yield has been determined: 
\[ \Phi_3(248 \text{ nm}, 298 \text{ K}, 1000 \text{ mbar air}) = 0.62 \pm 0.02, \]
which is the first reported data in the literature. The smaller-than-unity quantum yield indicates that photophysical processes also play a role in the mechanism.

4. A very significant OH formation has been observed for the reactions \( \text{C}_2\text{H}_5\text{CO} + \text{O}_2 \) and \( (\text{CH}_3)_3\text{CC(O)} + \text{O}_2 \) at low pressures. At around 1 mbar reaction pressure, the OH yield (branching ratio) is close to unity, as for instance in the case of the propionyl radical reaction it is \( \Gamma_{3b}(1.37 \text{ mbar He}) = 0.88 \pm 0.06 \). The OH yield decreases rapidly with increasing pressure, as for instance at 13.34 mbar: \( \Gamma_{3b} = 0.33 \pm 0.03 \). The observed pressure dependence is understood by a „chemical activation” mechanism occurring through the formation of a vibrationally excited acyl-peroxy radical. As a result of the OH-yield investigations, the rate coefficients for the OH + propionaldehyde (8) and OH + pivalinaldehyde (9) have also been determined, which are the following: 
\[ k_8(298 \text{ K}) = (1.85 \pm 0.06) \times 10^{-11}, \]
and 
\[ k_9(298 \text{ K}) = (2.65 \pm 0.17) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]
[2],[4],[6]

5. All OH reactions that have been dealt with proceed via hydrogen abstraction. The determined rate coefficients lie in a wide range comprising more than 3 orders of magnitude in the range of \( k_2 \approx 7 \times 10^{-15} – k_9 \approx 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The relative magnitudes of the rate coefficients of OH with the studied substrates are the following at room temperature: 
\[
\begin{align*}
\text{C}_2\text{H}_4\text{F} & : \text{CH}_3\text{C(O)F} : \text{CF}_2\text{COOH} : \text{C}_2\text{H}_5\text{C(O)H} : (\text{CH}_3)_3\text{CC(O)H} = 1 : 3.47 \times 10^{-2} : 0.82 : 86.85 : 124.4
\end{align*}
\]
The great difference in reactivity is understood by the electrophilic nature of the OH radical, the strong negative inductive effect of the fluorine substituents, the electron donating effect of alkyl
substituents, as well as thermochemical reasons. As for instance, the combined electron withdrawing effect of the F-substituent and that of the carbonyl group explains the unusually low rate coefficient of the OH + acetyl-fluoride reaction, while the small bond dissociation energy of the aldehydic C–H bond explains the very large k-values of the studied OH + aldehyde reactions. [2],[4],[6]

6. The acetonyl radical (CH₃C(O)CH₂) reacts with Br₂ with a relatively slow rate compared, for example, by the alkyl radical + Br₂ reactions. The room temperature rate coefficient is \(k_{7}(298 \text{ K}) = (2.33 \pm 0.02) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\); the rate coefficient increases slightly with increasing temperature. The reduced reactivity of the acetonyl radical can be explained by its resonance stabilized molecular structure.

7. The rate coefficient of the reaction of bromine atom with ethane was not known previously at ambient temperature. A rate coefficient value of \(k_{10}(310 \text{ K}) = (3.78 \pm 0.50) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) has been proposed by the current study. The \(k_{10}\) rate coefficient has been utilized to estimate the standard enthalpy formation value of the ethyl radical of \(\Delta fH_{298}^{o}(\text{C}_2\text{H}_5) = (122.0 \pm 1.9) \text{ kJ mol}^{-1}\), which agrees well with the generally accepted value. [1],[5]

8. The atmospheric lifetime of acetyl fluoride \(\pi(\text{CH}_3\text{C(O)F}) = 368 \text{ days} \approx 1 \text{ year}\) has been proposed by the determined reaction kinetic and photochemical parameters, as well as literature data. The atmospheric lifetime of acetyl-fluoride is not significantly longer than that of its parent molecule C₂H₅F (HFC-161). Therefore, it can be concluded that HFC-161 is not only a very low GWP refrigerant, but also that its atmospheric degradation probably does not contribute to global warming or cause other environmental problems.
5. Possible Practical Applications

Global warming and its likely grave effects on the Earth’s ecological systems present one of the greatest threats facing mankind the coming decades. The UN’s International Panel on Climate Change in its latest evaluation report (IPCC 2007) has unequivocally concluded that the main reason of climate change is due to human activity. First of all, to the increased use of fossil fuels that release the most important greenhouse gas (GHG), carbon dioxide in the atmosphere. The reduction of CO$_2$ emission is, however, very expensive, it may cause social and economic problems, and there are more and more indications that the restrictive measures have not been implemented to the needed extent.

It is relatively little known that the climatic effect of the chemically active greenhouse gases in the atmosphere amounts to about half of that of CO$_2$. The reactive GHGs include the air conditioning agent HFC’s and the tropospheric ozone which is also a toxic gas, a main component of the urban smog. These belong to the subjects where atmospheric chemistry research can contribute to the mitigation of climate change.

Thus, it is understood that one of the most important aspects of the development of air conditioners is the reduction of their GWP values. The GWP of HFC-161 (C2H5F) is much smaller that of the generally used HFC refrigerants. It was not known, however, if the atmospheric degradation of HFC-161 would lead to the formation of strong greenhouse gases or compounds harmful to the environment. My PhD study has provided a convincing positive answer for both of these two questions. The studied carbonyl molecules and carbonyl free radicals play an important role in the formation of tropospheric ozone.

The rate coefficients, absorption cross sections and photodissociation quantum yields determined in laboratory experiments can be used in atmospheric chemistry models. The performance of these models is basically determined by the reliability of the kinetic and photochemical data that are used as input parameters in the models; the outcome of computer simulations can be compared with the results of atmospheric field measurements. The laboratory experiments, modelling studies and atmospheric field measurements together contribute to a better understanding of the complex chemistry of the atmosphere providing a basis for scientifically sound predictions. Parts of the kinetic and photochemical results presented in my PhD have already been utilised in atmospheric modells in the framework of the European atmospheric chemistry project SCOUT-O3.

Publications Directly Related to the PhD Thesis


Proceedings Directly Related to the PhD Thesis


Other Publications


**Publications Prepared for Submission**

10. Gábor L. Zügner, Emese Szabó, Sándor Dóbé, Dariusz Sarzyński, Katarzyna Brudnik and Jerzy T. Jodkowski: *Experimental and theoretical study of the reaction of acetonyl radical (CH$_3$C(O)CH$_2$) with Br$_2$* Chem. Phys. Letters, (prepared for publication, the expected date of submission: 2012)

11. Gábor L. Zügner, Mária Farkas, István Szilágyi, Dariusz Sarzyński, Sándor Dóbé, Xinli Song and Baoshan Wang: *Experimental and theoretical study on the atmospheric fate of HFC-161 (C$_2$H$_5$F) and its degradation intermediate acetyl-fluoride (CH$_3$C(O)F)* Chem. Phys., (prepared for publication, the expected date of submission: 2012)

**Lecture in English**


**Lectures in Hungarian**


15. A globális klímaváltozás hatása szerves halogénmolekulák légkörkémiajára és fotokémiajára, Zügner Gábor László, *MTA fiatal kutatók szakbizottsági meghallgatása* (Budapest, 18th September 2009.)


20. Competitive Bromination Kinetic Study of \( \text{C}_2\text{H}_6 \), \( \text{CH}_2\text{CIBr} \) and neo-\( \text{C}_3\text{H}_{12} \). Reaction Kinetics and Thermochemical Implications, T. Bérces, F. Mátra, R. Nádasdi, I. Szilágyi, J. Zádor, G. Zügner, S. Dóbé, Third European Combustion Meeting, 2007, Chania, Crete.


34. OH Reaction Kinetics of the Biofuel Molecules \( \gamma \)-Valerolactone and Ethyl Levulinate, M. Farkas, A. Illés, B. Petri, D. Zsibrita, G. L. Zügner, S. Dóbe, COST 2nd Annual Meeting 2011, Zaragoza, Spain

35. Experimental and Theoretical Study of the Reactions of \( \text{C}_2\text{H}_5\text{CO} \) and \( \text{CH}_3\text{CHC(O)H} \) radicals with \( \text{O}_2 \), G.L. Zügner, I. Szilágyi, J. Zádor, S. Dóbé, X. Song and B. Wang, Magyar Égéstudományi Bizottság ülése, 2011, Miskolc