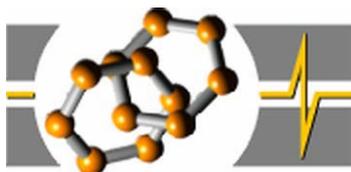# Reaction Kinetics and Photochemical Study on the Atmospheric Fate of Selected Fluoro-Organics and Carbonyl Molecules

Summary of PhD Thesis

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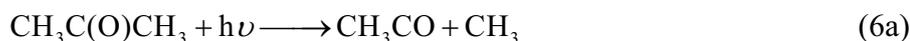Supervisor: Sándor Dóbé, DSc., Head of Department

INTRODUCTION

One of the greatest environment problems facing mankind is the depletion of the Earth's protecting ozone layer and the global warming both of which can be attributed to the recent change of the composition of the atmosphere. The chemical processes occurring in the atmosphere, combustion processes and the synthesises of chemical industry, all are complex chemical changes that are build-up of elementary reactions. In order to understand the complex chemical systems, it is of vital importance to know the rate constants and photodissociation quantum yields of the elementary chemical and photochemical reactions that comprise the reaction mechanism.

Different computer models have been widely used to describe the complex chemical and physical processes of the atmosphere. The reliability of these models, beside the mechanism itself, is determined basically by the accuracy of the rate coefficients and quantum yields of the elementary chemical and photochemical reactions entering the mechanism.

The different theories of chemical kinetics deal with the description and understanding of chemical reactions at the molecular level and the calculation of kinetic parameters of elementary reactions. The modern science of reaction kinetics is based in a great part on the knowledge of experimental studies performed by direct kinetics methods. The reliable kinetic data allow supplied by such experiments the possibility to test and develop the different theories of chemical kinetics.

In my PhD thesis I report reaction kinetics and photochemical experimental studies of elementary chemical and photochemical reactions in the gas phase that are the focus of basic research and at the same time are of practical importance as well. The following reactions have been investigated:

$$CH_3CH_2OH + OH \longrightarrow products \qquad k_1 \qquad\qquad (1)$$

$$CF_2HCH_2OH + OH \longrightarrow products \qquad k_2 \qquad\qquad (2)$$

$$CF_3CH_2OH + OH \longrightarrow products \qquad k_3 \qquad\qquad (3)$$

$$CH_3C(O)F + OH \longrightarrow products \qquad k_4 \qquad\qquad (4)$$

$$CH_3C(O)CH_3CH_2 + OH \longrightarrow products \qquad k_5 \qquad\qquad (5)$$

$$CH_3C(O)CH_3 + h\upsilon \longrightarrow products \qquad \Phi_6(\lambda,p,T,M) \qquad (6)$$

$$CH_3C(O)CH_3 + h\upsilon \longrightarrow CH_3CO + CH_3 \qquad\qquad (6a)$$

$$CH_3CO + O_2 \longrightarrow products \qquad\qquad (7)$$

$$CH_3CO + O_2 \longrightarrow OH + products \qquad \Gamma_{7a} = k_{7a}/k_7 \qquad (7a)$$

$$CH_3CO + HBr \rightleftharpoons CH_3C(O)H + Br \qquad k_8,\ \Delta_f H^{\circ}_{298}(CH_3CO) \quad (8,-8)$$

The studied reactions can be divided into two groups. In the first group, (1-5), there are the reactions of OH radicals with molecules that are of importance in atmospheric chemistry. The second group contains the photolysis reaction of acetone (6) and the reactions (7-8) of the acetyl radicals (CH_3CO) that are products in the photodissociation of acetone.

EXPERIMENTAL

In the experimental work I have applied several methods and procedures that are best suited for the study of the respective reactions. Development of some of the experimental techniques has been accomplished as part of my present PhD work.

Most of the reactions have been investigated by applying direct kinetics methods. Common in the direct techniques is that the atoms or free radicals that are either consumed or formed in the reactions are observed directly and at the "real" time-scale required by the

elementary reaction steps. The experiments have always been carried out under pseudo-first-order conditions with large excess of the stable reactants. Under such conditions, the reactions studied have been found to obey first order kinetics with single exponential decay of the free radicals.

Reactions (1-3) and (8) have been investigated in photolytic systems where the free radicals (OH or CH_3CO) are produced by pulsed laser photolysis (LP) of suitable precursors (in most cases HNO_3 or $CH_3C(O)CH_3$). The time history of OH-radicals in the reactions has been followed by resonance fluorescence (RF) detection, while that of the acetyl radicals by using transient absorption (TA) spectrometry.

Reactions (4-5) and (7) have been studied with the discharge flow (DF) method by producing the radicals via fast gas titration reactions of atoms formed in microwave discharge attached to an isothermal flow tube. In the DF system, the reaction time is set by the distance between the place of mixing of the reactants and the detection port, as well as the flow velocity. Time resolution is achieved by varying the mixing distance relative to the detection site. In the DF experiments, RF monitoring of OH was applied in most cases, but for reaction (7), the more sensitive laser induced fluorescence (LIF) detection was used.

As part of the present doctoral work a new method of pulsed laser photolysis coupled with gas-chromatographic analysis (LP/GC) has been developed and applied to determine the consumption quantum yield of acetone (Φ_6). The method involves the measurement of the loss of acetone as a result of laser irradiation with known number of laser shots and energies ($n\ E$). The irradiated samples always contained O_2 in order to trap the free radicals formed in the photolysis of acetone. The possible systematic errors have been assessed in separate experiments in order to optimize the experimental parameters.
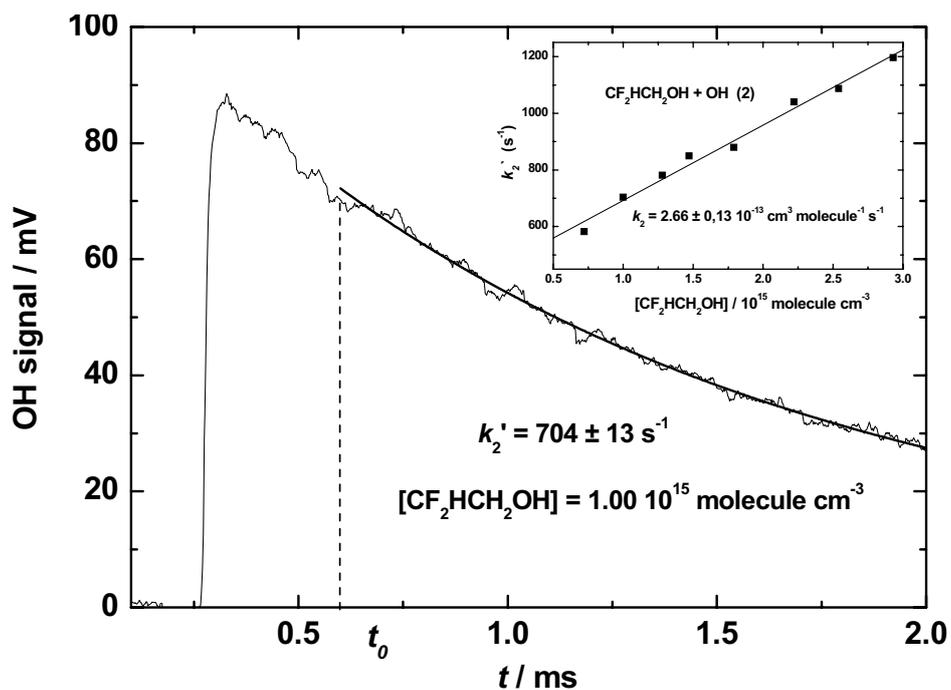
Figure 1. Representative OH concentration profile measured in one of the LP/RF experiments. The inset shows the determination of the bimolecular rate coefficient for the reaction.
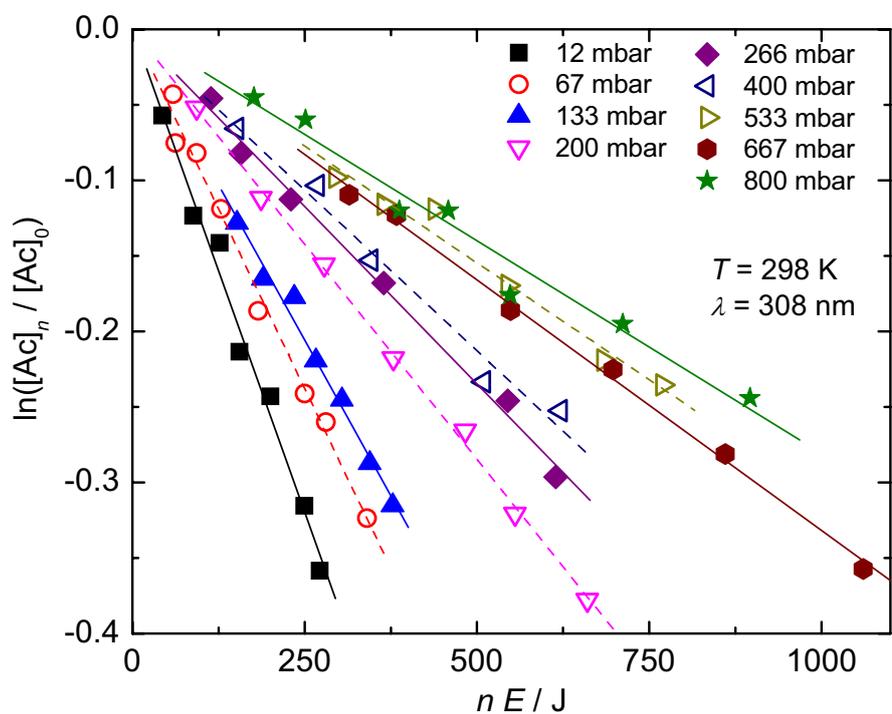

Figure 2. Determination of the photodissociation quantum yield for acetone at different pressures in synthetic air. The slopes of the straight lines of the semilogarithmic plots are proportional to Φ_6.

NEW SCIENTIFIC RESULTS

Kinetics of OH-reactions studied

1. The pulsed laser photolysis experimental method with resonance fluorescence detection has been developed for the investigation of the effect of F-substitution in the reaction of OH radicals with fluoro-alcohols. The following rate coefficients have been determined: k_1 (300 K) = (3.8 ± 0.0) 10^{-12} , k_2 (300 K) = (2.2 ± 0.2) 10^{-13} és k_3 (300 K) = (1.6 ± 0.5) 10^{-13} cm^3 molecule^{-1} s^{-1}. The rate coefficient for the reaction CF_2HCH_2OH + OH (2) is the first reported value obtained by a direct experimental method.

2. The rate coefficients determined for reactions CF_2HCH_2OH + OH (2) and CF_3CH_2OH + OH (3) have been applied for estimating the atmospheric lifetime of the two fluoro-ethanols. These are the following: τ(CF_2HCH_2OH) = 58 days and τ(CF_3CH_2OH) = 95 days.

3. Kinetics of the reaction acetyl-fluorine + OH (4) have been studied in a fast flow system with RF detection of OH. The rate coefficient value of k_4 (300 K) = (7.40 ± 0.48) 10^{-15} cm^3 molecule^{-1} s^{-1} has been determined which is the first direct kinetic data for this reaction. A group-reactivity factor (SAR) of F(C(O)F) = 0.054 has been derived by utilizing the above rate coefficient as a first value reported in the kinetic literature.

4. Kinetic investigations of the reaction of methyl-ethyl-ketone (MEK) with OH radicals are of importance from chemical kinetics and atmospheric chemistry point of view as well. Applying the DF/RF method k_5 (297 K) = (1.09 ± 0.09) 10^{-12} cm^3 molecule^{-1} s^{-1} rate coefficient value has been determined for this reaction. Up to now, k_5 has been measured in photolytic systems only.

5. All of the OH-reactions studied (1-5) occur via H-atom abstraction. The rate coefficients of the reactions decrease with the increasing bond dissociation energy of the C–H bond under attack. This trend is influenced, however, by the inductive effect of the substituents in accordance with the known electrophilic nature of the OH radical. As for instance, ethanol reacts about 14-times faster than ethane with the OH-radical which is a consequence of the weaker secondary C–H bond and the electron donating property of the OH-group. Similarly, MEK contains a CH$_2$-group which is attached to the electron donating methyl moiety. This explains why the reaction of OH with MEK is about 6-times faster compared with the acetone reaction. The reduced reactivity of the fluorinated molecules studied is caused by the effect of the electron withdrawing F-atoms that reduce the electron density on the H-atoms to be abstracted and therefore diminish the rates of the electrophilic OH-reactions. The effect is significant as it is seen by the following ratios: $k(CH_3CH_2OH + OH) / k(CF_3CH_2OH + OH) \approx 32$ and $k(CH_3C(O)CH_3 + OH) / k(CH_3C(O)F + OH) \approx 23$ (T = 298 K).

6. The photochemistry of acetone has been studied the most of the organic molecules, but recently new aspects have emerged after the recognition of the important role that acetone plays in the chemistry of the atmosphere. A novel method of pulsed laser photolysis coupled with gas-chromatographic analysis has been developed and applied for the determination of the consumption quantum yield (QY) of acetone. As a test of the experimental method it has been verified that the Φ_6 value for acetone is unity and independent of the overall pressure at 248 nm photolysis wavelength.

7. It has been concluded that QY of acetone decreases significantly with decreasing temperature at 308 nm photolysis wavelength. These results contradict the previous data and the IUPAC recommendation. On the other hand, they confirm the very recent findings of a British research group[1] obtained by an entirely different experimental method.

T K	Φ_6(33 mbar)	Φ_6(133 mbar)
348	0.65 ± 0.06	0.42 ± 0.04
298	0.53 ± 0.02	0.32 ± 0.02
273	0.41 ± 0.02	0.24 ± 0.01
253	0.35 ± 0.04	0.19 ± 0.02
233	0.31 ± 0.02	0.12 ± 0.01

Table 1. The photolysis quantum yield of acetone at different pressures in synthetic air.

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[1] [Blitz 2004] Blitz, M. A.; Heard, D. E.; Pilling, M. J.; Arnold, S. R.; Chipperfield, M. P., *Gheophys. Res. Lett.,* **2004**, *31,* L06111.

8. The pressure dependence of acetone QY has been determined in a wide range of pressures at 308 nm in synthetic air at room temperature (T = 298K). The quantum yields display substantial pressure dependence, e. g., Φ_6(13 mbar) = 0.581 ± 0.032 and Φ_6(1000 mbar) = 0.112 ± 0.004 have been measured at the lowest and highest pressures, respectively. The experimental data have been found to show nonlinear dependence in Stern-Volmer plot, ($p - \Phi_6^{-1}$), characterized by two different slope parts of the plot. The $p - \Phi_6^{-1}$ values obtained agree well with those of the respective data reported by Blitz et al[1].

9. The effect of buffer gases on acetone QY have been studied, besides synthetic air, also in He, Xe and O_2 at room temperature (λ = 308 nm). The quantum yields have been found to vary significantly with the quenching gases e. g. Φ_6(400 mbar O_2) = 0.181 ± 0.010, Φ_6(400 mbar air) = 0.193 ± 0.017, Φ_6(400 mbar Xe) = 0.226 ± 0.009 and Φ_6(400 mbar He) = 0.278 ± 0.005 (T = 298K). The pressure dependence for all buffer gases displays nonlinear Stern-Volmer behaviour.

10. A new mechanism for the photodissociation of acetone at 308 nm has been proposed by utilizing literature sources as well. In this mechanism, the photodissociation occurs from both the excited singlet and triplet states. The proposed mechanism explains the observed pressure dependence and it is in accordance with the different quenching efficiency of the buffer gases used in the experiments.

11. Aloisio and Francisco[2], have recently reported a very significant effect of water on the QY of acetone. In the current study, no such effect could be established. It has been

[2] [Aloisio 2000] Aloisio, S.; Francisco, J. S., *Chem. Phys. Lett.,* **2000**, *329,* 179.

concluded that at both 248 and 308 nm wavelengths, the QY of acetone agrees within error margins in the presence and absence of water.

12. It has been shown by experiments conducted in thermal (DF) systems that the reaction of acetyl radicals with O_2 can not occur just by simple association, it proceeds rather by a "chemical activation" mechanism in which as one of the products OH radical is formed. A lower limit for the branching ratio ($\Gamma_{7a} = k_{7a} / k_7$) of the OH-forming channel of $\Gamma_{7a} > 0.32$ has been estimated by the experiments $p \leq 3.6$ mbar. This appears to be the first quantitative result for the branching ratio of reaction (7a) reported in the literature.

13. The rate coefficient value of k_8 (298 K) = (3.59 ± 0.23) 10^{-12} cm^3 molecule^{-1} s^{-1} has been determined for the reaction of acetyl radicals with HBr by applying the pulsed laser photolysis experimental technique with transient absorption monitoring of CH_3CO. This rate coefficient, together with k_{-8} taken from the literature, has been utilized in the so called "third law analysis" procedure to obtain the standard molar enthalpy of formation value of $\Delta_f H^\circ_{298}(CH_3CO) = -10.04 \pm 0.55$ kJ mol^{-1}. This enthalpy of formation translates to the acetone photodissociation threshold wavelength of $\lambda_{th} = 338$ nm (reaction (6a)).

PRACTICAL APPLICATIONS

The fluorinated alcohols have recently been recommended as substitutes for freons. The fate and therefore the atmospheric lifetime of fluoro-alcohols emitted into the atmosphere is determined basically by oxidative degradation reactions initiated by hydroxy radicals. In this case the rate coefficients determined from laboratory reaction kinetics measurements directly supply information on the atmospheric fate of the studied molecules. The rate coefficient k_2 and k_3 determined in the present study indicate that the fluoro-ethanols studied are characterized by a relatively short lifetime in contrast, e. g., with freons that deplete 2-3 orders of magnitude slower. It has been concluded that the practical applications of 2,2-difluoro-ethanol and 2,2,2-trifluoro-ethanol are likely not to cause environmental problems.

Acetone is one of the most abundant organics occurring in the atmosphere. The photodissociation of acetone takes place already at the relatively long wavelengths that reach the troposphere producing reactive free radicals in the primary photochemical steps and via photochemical oxidation. After the recognition of global warming, the complex interaction between chemistry and climate has become the focus of research interest. The current work performed at the Reaction Kinetics Department has been part of an EU Integrated Project SCOUT-O3[3]. In this comprehensive atmospheric chemistry project, laboratory experiments, field measurements and computer modeling studies have been in progress. In the present work, the photodissociation quantum yield of acetone has been concluded to decrease with decreasing temperature. This result confirms a very recent proposal and has been included in global atmospheric chemistry models. The new modeling studies have revealed that the lifetime of acetone in the upper troposphere is about 3-times larger than that was thought before when the calculations were made by assuming temperature independent QYs. This

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[3] http://www.ozone-sec.ch.cam.ac.uk/scout_o3/

means that the contribution of acetone photolysis to the budget of OH and HO_2 radicals is reduced one-half to one-fourth of the previous recommendation.

LIST OF PUBLICATIONS

Publications directly related to the PhD thesis:

Kovács, Gg., **Kinetics and photochemical study on the atmospheric fate of fluoro Alcohols and Acetone**, *Periodica Polytechnica, Ser. Chem. Eng.*, **2005**, *49*, 59.

Imrik, K.; Kovács, Gg; Fejes, I.; Szilágyi, I.; Kovács, G.; Dóbé, S.; Bérces, T.; Márta, F.; **Kinetic studies of Br atom reactions. Determination of enthalpies of formation for free radicals of combustion importance**, *Proceedings of the European Combustion Meeting*, **2005,** 58.

Kovács, Gg.; Dóbé, S.; Farkas, E.; et al., **General discussion**, *Faraday Discuss.*, **2005**, *130*, 125.

Kovács, Gg.; Bencsura, Á.; Dóbé, S.; Bérces, T.; Márta, F., **Rate constant for the reaction $CH_3CO + HBr$ and the enthalpy of formation of the CH_3CO radical**, *React. Kinet. Catal. Lett.*, **2005**, *86*, 355.

Kovács, Gg.; Szász-Vadász, T.; Papadimitriou, V. C.; Dóbé, S.; Bérces, T.; Márta, F., **Absolute rate constants for the reaction of OH with CH_3CH_2OH, CF_2HCH_2OH and CF_3CH_2OH**, *React. Kinet. Catal. Lett.*, **2006**, *87*, 129.

Presentations directly related to the PhD thesis:

Kovács Gergely, **2,2-difluor-etanol hidroxilgyökkel végbemenő reakciójának kinetikai vizsgálata,** *Reakciókinetikai és Fotokémiai Munkabizottság ülése*, Gyöngyöstarján, 2002. október 30-31, *(lecture)*.

Kovács Gergely, **Az OH-gyök fluor-alkoholokkal végbemenő reakciójának kinetikai vizsgálata,** *Kutatóközponti Tudományos Napok*, MTA KK, Budapest, 2003. május 28-29, *(lecture)*.

Kovács Gergely, **Fluor-alkoholok és aceton légkörkémiailag fontos reakcióinak és fotokémiájának vizsgálata**, *2. Doktoráns Konferencia*, BME Vegyészmérnöki Kar, Doktori Iskola, BME, Budapest, 2004. november 24, *(lecture)*.

Kovács Gergely, **Az aceton légköri fotokémiájáról**, *Reakciókinetikai és Fotokémiai Munkabizottság ülése*, Balatonalmádi, 2005. április 28-29, *(lecture)*.

Kovács Gergely, **Az aceton légköri fotokémiája**, *Kutatóközponti Tudományos Napok*, MTA KK, Budapest, 2005. június 1-2, *(lecture)*.

Krisztina Imrik, Gergely Kovács, István Fejes, István Szilágyi, Gábor Kovács, Sándor Dóbé, Tibor Bérces and Ferenc Márta, **Kinetic Studies of Br Atom Reactions. Determination of Enthalpies of Formation for Free Radicals of Combustion Importance**, *European Combustion Meeting*, Louvain-la-Neuve, Belgium, April 3-6, 2005, *(poster)*.

Edit Farkas, Gergely Kovács, Krisztina Imrik, Gábor Vasvári, István Szilágyi, István Fejes, Ákos Bencsura, Sándor Dóbé, Tibor Bérces and Ferenc Márta, **Kinetics and Photocemical Study on the Atmospheric Fate of Acetone**, *Faraday Discussion 130: Atmospheric Chemistry,* University of Leeds, UK, April 11-13, 2005, *(poster)*.

Other publications:

Farkas, E.; Imrik, K.; Szilágyi, I.; Kovács, Gg.; Dóbé, S.; Márta, F., **Polar effect in the reaction of CH_3O with HBr**, *React. Kinet. Catal. Lett.,* **2004**, *83*, 315.

Farkas, E.; Kovács, Gg.; Szilágyi, I.; Dóbé, S.; Bérces, T.; Márta, F., **Rate constant for the reaction of $CH_3C(O)CH_2$ radical with HBr and its thermochemical implication**, *Int. J. Chem. Kinetics,* **2006**, *38*, 32.

Imrik, K.; Kovács, Gg.; Szilágyi, I.; Fejes, I.; Sarzinsky, D.; Dóbé, S.; Bérces, T.; Márta, F.; Espinosa-García, J., **Absolute and relative-rate experiments and direct dynamics computations for the reaction of Br atoms with CH_2ClBr**, *J. Phys. Chem. A*, **2006**, accepted to publication.