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Summary of the Ph.D. Thesis by

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KINETIC STUDIES OF SELECTED ELEMENTARY REACTIONS OF ACETONE AND THE ACETONYL RADICAL OF RELEVANCE TO ATMOSPHERIC CHEMISTRY

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INTRODUCTION

Elementary reactions – the simplest type of chemical reactions – are basic constituents of the complex chemical processes. By studying of them one can understand more deeply such complex chemical systems as the Earth's atmosphere, industrial syntheses, combustion processes etc.

The study of elementary reactions belongs to the field of reaction kinetics. Nowadays, kinetics – in addition to determination of rate constants – deals for example, with studying the rate and mechanism of elementary reactions on the molecular level. This is made possible by the considerable development in experimental and theoretical methods over the past few years. Among the modern experimental techniques, the application of lasers is of particularly great importance.

The other major part of kinetics is the application of kinetic data which means computer modeling of complex chemical systems.

The aim of my research has been to study the kinetics of such elementary reactions that are particularly interesting from basic chemical kinetics reasons and are also important from a practical point of view.

My work deals with the kinetic studies of the following – *radical* + *molecule* and *radical* + *radical* type – gas-phase elementary reactions:

$$OH + CH_3C(O)CH_3 \rightarrow \text{products} \qquad (1)$$
$$OH + CH_3C(O)CH_3 \rightarrow CH_3C(O)CH_2 + H_2O \qquad (1a)$$

$$OH + CD_3C(O)CD_3 \rightarrow \text{products} \qquad (2)$$

$$CH_3C(O)CH_2 + O_2 \rightarrow \text{products} \qquad (3)$$
$$CH_3C(O)CH_2 + O_2 \rightarrow OH + CH_2CO + CH_2O \qquad (3a)$$

$$CH_3C(O)CH_2 + NO \rightarrow \text{products} \qquad (4)$$
$$CH_3C(O)CH_2 + NO_2 \rightarrow \text{products} \qquad (5)$$

$$CH_3C(O)CH_2 + H \rightarrow \text{products} \qquad (6)$$
$$CH_3C(O)CH_2 + HBr \rightarrow \text{products} \qquad (7)$$
$$CH_3O + HBr \rightarrow \text{products} \qquad (8).$$

EXPERIMENTAL METHOD

All experiments were carried out by using the thermal flow discharge (FD) technique, which is one of the direct experimental methods in reaction kinetics. Radicals (OH, $CH_3C(O)CH_2$ and CH_3O) were produced by fast gas-titration reactions. In most cases, the relative change in the concentration of the consumption or formation of free radicals was followed as a function of reaction time. Two optical detection methods were used to monitor the free radicals: resonance fluorescence (RF) and laser induced fluorescence (LIF). Excitation light sources were: „resonance lamp", XeF excimer laser (λ = 351 nm) and a dye-laser pumped by Nd:YAG laser.

Experiments to determine rate constants for the overall reactions were carried out by applying the so-called „on-off„ technique. This technique allowed the correction for heterogeneous wall consumption of radicals thus providing the pseudo-first order rate coefficient directly from the experiments.

I also used the „comparative" technique, which is based on the comparison of the product yields. It made possible to determine the yields (reaction branching ratios) by measuring relative radical concentrations.

All experiments were carried out under pseudo-first order conditions, in large excess of the reactant over the free radical, [reactant] >> [free radical]$_0$.

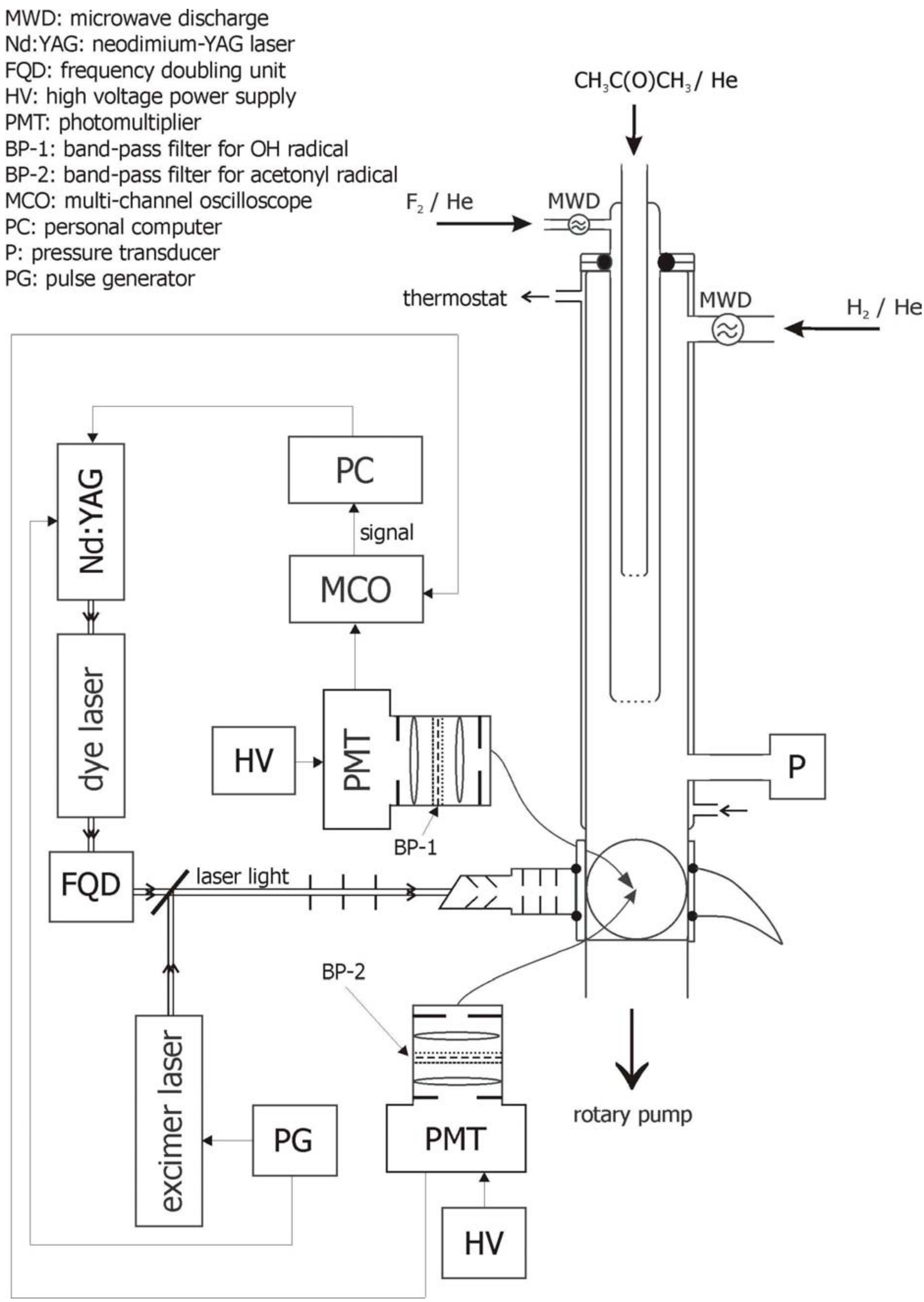

Figure 1. *Discharge flow system coupled with two kinds of LIF detection methods.*

NEW SCIENTIFIC RESULTS

Kinetics and Reaction Mechanism Study of the OH + Acetone Reaction

1. The temperature dependence of the rate coefficient of the OH + acetone overall reaction (1) was determined between 243 and 353 K (2.6 mbar He) – using thermal discharge flow system. It was established that the Arrhenius plot of k_1 is curved: under room temperature the rate coefficient hardly decrease with decreasing temperature. Hitherto the non-Arrhenius behaviour of the reaction (1) was established merely in photolytic systems.

2. Temperature dependence of the yield (branching ratio) of acetonyl formation of OH + acetone reaction (1a), $\Gamma_{1a} = k_{1a}/k_1$, was determined. The average yield of acetonyl – using two OH-sources: $F + H_2O$ and $H + NO_2$ – was measured to be $\Gamma_{1a} = (0.91 \pm 0.06(2\sigma))$ $(T = 283 - 343\ K)$ and $\Gamma_{1a} = (0.83 \pm 0.06(2\sigma))$ $(T = 253 - 299\ K)$. Γ_{1a} was found independent of temperature in the observed temperature range. Consequently, acetonyl radical is by far the main reaction product, in contrast with some previous literature data.

3. The effect of water on the OH + acetone reaction was studied in connection to a recent theoretical paper; investigations were carried out in the presence and absence of a high concentration of water. The conclusion from all sets of experiments is that there is no significant water effect on the overall kinetics as well as on the yield of the acetonyl radical of the OH + acetone reaction at room temperature.

4. The rate coefficient of the OH + acetone-d_6 reaction (2) was determined at 300 K and 2.66 mbar: $k_2\,(300\ K) = (3.24 \pm 0.23(2\sigma))\ 10^{-14}$ $cm^3\ molecule^{-1}\ s^{-1}$. Using my previous experimental results, the kinetic isotope effect (KIE) was also calculated and was found to be large: $KIE = (k_{OH + acetone} / k_{OH +\ acetone\text{-}d_6}) = (5.4 \pm 0.5(2\sigma))\ \ (T = 300\ K)$.

Kinetic Study of Selected Elementary Reactions of the Acetonyl Radical

5. The reaction of acetonyl radical with O_2 is a typical type of recombination-decomposition reactions. The pressure dependence of its rate coefficient was studied – with direct kinetic method – at the low pressure rang, between 1.3 - 10.6 mbar (He), at room temperature. By fitting the experimental data – i.e. the bimolecular rate coefficients vs. overall pressure – the low pressure limiting rate coefficient of $k_{3,0} = (4.14 \pm 0,55(2\sigma))\ 10^{-29}\ cm^6\ molecule^{-2}\ s^{-1}$ was obtained. It is believed to be more reliable than the previous literature data [Oguchi 2001].

6. The possible formation of OH radical in the reaction of the acetonyl radical with O_2 (3a) was studied at 298 K and 2.84 mbar. The formation of OH radical in the reaction (3a) is negligible, $\Gamma_{3a} \leq 0.04$.

7. For the reactions of the acetonyl radical with nitrogen monoxide (4) and nitrogen dioxide (5) the following rate coefficients were derived at room temperature (p = 2.85 mbar): $k_4(298\ K) = (1.04 \pm 0.19(2\sigma))\ 10^{-11}$ and $k_5(298\ K) = (3.25 \pm 0.65(2\sigma))\ 10^{-11}$, both in $cm^3\ molecule^{-1}\ s^{-1}$.

8. The kinetics of the acetonyl radical + H reaction (6) was studied at room temperature and 2.85 mbar pressure. Reaction (6) is an extremely fast

one and only a lower limit could be assessed for its rate constant: $k_6(298\ K) \geq 3\ 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$.

9. The structure-reactivity relationship for the acetonyl radical was studied by comparing my results with literature data. With the exception of the O_2 reaction (3), it can not be claimed that the resonance stabilization of the acetonyl radical leads to a reduced reactivity. It has been found that the acetonyl radical shows a very similar reactivity to allyl radical contrary that the allyl radical possesses a much higher degree of electron delocalization.

10. The rate coefficient of the acetonyl radical + HBr reaction (7) was determined at 298 K and 2.66 mbar: $k_7(298\ K) = (3.04 \pm 0.20(2\sigma))\ 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$.

11. By making use of own kinetic result k_7(298 K) the heat of formation of the acetonyl radical was estimated. Getting the rate coefficients of the „reverse reaction" from the literature, the following values were derived: $\Delta_f H^o{}_{298}(CH_3C(O)CH_2) = (-24.3 \pm 5.8(1\sigma))$ and $\Delta_f H^o{}_{298}(CH_3C(O)CH_2) = (-28,. \pm 3.1(1\sigma))$ in $kJ\ mol^{-1}$.

12. The rate coefficient of the CH_3O + HBr reaction (8) was determined at room temperature and 2.30 mbar: $k_8(298\ K) = (1.40 \pm 0.27(2\sigma))\ 10^{-12}\ cm^3\ molekula^{-1}\ s^{-1}$. The reaction (8) is by far the fastest reaction among the hydrogen abstraction reactions of CH_3O radical at room temperature, which can be explained by the polar structure of the transition state.

POSSIBLE APPLICATION

In addition to the chemical kinetics interest, most of the reactions studied have atmospheric implications as well. The kinetic data that have been determined and also the heat of formation of the acetonyl radical can be applied in atmospheric computer models.

PUBLICATIONS

Publications in the Subject of the Thesis:

1. Vasvári G., Szilágyi I., Bencsura Á., Imrik K., Farkas E., Dóbé S., Bérces T., E. Henon, S. Canneaux, F. Bohr: **Reakció és komplexképződés OH-gyök és aceton között**, *XXIII. Országos Lumineszcencia Spektroszkópia Konferencia*, 2000. október 19-21. Szerkesztő: Marek Nándor és Szabó Klára, Pécs, 72. oldal, (2001).

2. E. Farkas, I. Szilágyi, S. Dóbé, T. Bérces, F. Márta: **Kinetic Isotope Effect in the Reaction of OH Radical with Acetone-d_6**, *React. Kinet. Catal. Letters*, 80, 351, (2003).

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

4. K. Imrik, E. Farkas, G. Vasvári, S. Dóbé, I. Szilágyi, D. Sarzinsky, T. Bérces, F. Márta: **Laser spectrometry and kinetics of selected elementary reactions of the acetonyl radical**, *Phys. Chem. Chem. Phys.*, 6, 3958, (2004).

5. E. Farkas, Gg. Kovács, I. Szilágyi, S. Dóbé, T. Bérces, F. Márta: **Rate constant for the reaction of $CH_3C(O)CH_2$ radical with HBr and its thermochemical implication**, *Int. J. Chem. Kinetics*, Accepted on 26-th of May, 2005.

Other Publication:

6. S. Dóbé, K. Imrik, I. Szilágyi, Á. Bencsura, E. Farkas, T. Bérces: **Heats of Formation for Free Radicals of Combustion Importance Determined by Reaction Kinetics Measurements**, *Proc. of the 4th Japan – Central Europe Joint Workshop on Energy and Information in Non-Linear Systems*, Brno (CR), November 10-12, (A. Gottvald, Ed.), p. 246, (2001).

Oral Presentations and Posters Presented on International Conferences:

1. Farkas E.: **Az OH-gyök reakciója acetonnal**, V. Doktori Kémiai Iskola, Királyrét, 2002. május 21-22. (Presentation)

2. Farkas E.: **Az OH-gyök reakciója acetonnal**, MTA-KK Tudományos Napok, Budapest, 2002. május 27-28. (Presentation)

3. K. Imrik, G. Vasvári, E. Farkas, I. Szilágyi, D. Sarzynski, S. Dóbé, T. Bérces and F. Márta: **Kinetic and Laser Spectrometric Study of the Acetonyl Radical**, *17th International Symposium on Gas Kinetics*, August 24-29, 2002, Essen, Germany. (Poster)

4. E. Farkas, Gg. Kovács, K. Imrik, G. Vasvári, I. Szilágyi, I. Fejes, Á. Bencsura, S. Dóbé, T. Bérces, F. Márta: **Kinetics and photochemical study on the atmospheric fate of acetone**, *Faraday Discussion 130 – Atmospheric Chemistry*, P41, April 11-13, 2005, Leeds, United Kingdom. (Poster)