Summary of the Results of Project No. K108966
Komplexképződéssel járó elemi reakciók kinetikájának leírására alkalmas elméleti módszerek fejlesztése

Complex formation is a widely observed phenomenon in chemistry. In this project, theoretical methods have been applied to learn details on two such phenomena: kinetics and dynamics of complex-forming bimolecular reactions, mostly in the gas phase, involving method development, as well as formation of host-guest and transition metal complexes. In the former studies, new theoretical methods have been developed and applied. The rate coefficients of several gas-phase reactions have been calculated, and their dynamics has also been characterized. This has been the main thrust of the proposal. The properties and kinetics/ mechanisms of the formation of transition metal complexes synthesized by our experi–mentalist collaborators have been described. This part of the project got more emphasis than it was planned, because the method development for the quantum chemical characterization of complexes, which was part of the proposal, proved to be unsuccessful. In the following, the results achieved in these fields will be summarized, followed by a brief overview of the personnel involved in the project, including the achievements of the young collaborators.

1. Method development

We intended to use the quasiclassical trajectory (QCT) method for the simulation of the dynamics of complex-forming bimolecular reactions, and assess the applicability of reduced-dimensional (RD) quantum dynamical methods for this purpose.

1.1. QCT calculations of dynamical characteristics of chemical reactions involve averaging over numerous parameters of the initial conditions of trajectories, in other words, calculation of multiple integrals. To facilitate the evaluation of such integrals, the Monte Carlo method is used. This means that the initial conditions are selected randomly from the available possibilities. For polyatomic molecules, a method called normal mode sampling is used for the generation of ensembles of semiclassically quantized classical states. In this method, the energies of the desired quantum states of the normal modes of a reactant molecule are determined using the quantum mechanical formula, from which the maximum displacement of the mode is determined. Then, a random phase is assigned to each oscillator, from which the values of the normal mode coordinates and momenta are calculated, which are converted to Cartesians. In this step some spurious center-of-mass momentum and some also unphysical angular momentum is generated, which can be eliminated with proper projections. This way, a random ensemble of classical states corresponding to the selected quantum state is obtained. Then trajectories describing the individual collisions with a partner are integrated. This means the members of the ensemble, while are generated with the assumption that the normal modes are separable and harmonic are suddenly placed on the real, anharmonic potential energy surface of the reactant molecules. The ensemble will adapt to the anharmonicities, i.e. the entire ensemble evolves during the initial part of the collisions, when the interaction between the reactants is still negligible. We have demonstrated that this evolution can be concerted, i.e. the individual members of the ensemble evolve coherently. As a result, the outcome of the set of collision trajectories will depend on how long time is available for the initial evolution of the ensemble of initial states. We have shown [1] that this can lead to unphysical results, for example, the calculated reaction probability can oscillate as a function of the initial separation of the reactants. If the amplitude of such oscillations is significant, there will be significant ambiguity in the calculated reactivity parameters. We designed a method, called one-period averaging [1], which can help one to avoid such uncertainties.

1.2. A different remedy to the problem of oscillation or systematic change of calculated reactivity parameters can be based on the adiabaticity principle of Ehrenfest (for references of the relevant literature, see Ref. 2). The latter states that if one has a semiclassically quantized state of a system of oscillators in some well-behaved model (such as vibrations of molecules in the harmonic approximation), then, according to the adiabatic theorem of classical mechanics, the system remains in the same quantum state when the potential energy is adiabatically switched from harmonic to anharmonic. The principle holds exactly for one-dimensional systems (except when discontinuities or bifurcations appear), but can be assumed to also work in multidimensional systems. One- and two-dimensional models of vibrating molecules have been well studied in the 1980s and 90s, but for polyatomic molecules, no successful applications have been reported, except for one recently published by Bowman et al. We have developed a method and computer code for the purpose, and demonstrated that, although bifurcations are possible during the switching, ensembles of such trajectories are consistent and reproduce the quantum sate energies of polyatomic molecules calculated by exact quantum mechanical methods [**Error! Bookmark not defined.**]. The extension of the method is in progress.

1.3. Using the earlier and the new method, we have investigated the accuracy of the Palma-Clary reduced-dimensional model of reactions involving a tetrahedral penta-atomic molecule (usually methane) and an atom. We developed a method [3] and a code for classical reduced-dimensional calculations corresponding to the Palma-Clary model for atom + tetrahedral penta-atomic molecule reactions. We found for the test reaction of methane with an H atom [4], that the qualitative picture provided by the model is correct, but there may be significant quantitative inaccuracy depending on the collision energy and the isotopolog. The application of the RD code to complex-forming bimolecular reactions is in progress.

2. Dynamics of individual reactions

We have studied two classes of complex-forming bimolecular reactions: those involving three atoms, and some involving four or more atoms. The reactions of the former class include the reactions of O-atom exchange going through the ozone as complex, $O' + O_2 \rightarrow O'O + O$, $H + O_2$ (the latter in electronic ground or first excited state) and NCN decomposition (the reverse of $C + N_2$). Among the reactions involving complexes formed by more than three atoms the following have been studied: OH + HBr, $O_2 + O_2$ (both singlet excited), CH_3 + HBr and $CH_3CHCHCH_2 + O_2$. In the following, we briefly summarize our results.

2.1. Two groups (those of Y. T. Lee in Taiwan and T. Minton in Montana, USA) performed crossed molecular beam experiments on $O' + O_2$ collisions, using isotope labeling. The collision energy in the experiments of the former group was relatively low, 5 to 7 kcal/mol, while the latter group used hyperthermal collisions energies (around 3 eV, 70 kcal/mol). In order to interpret their findings, we performed quasiclassical trajectory calculations and derived experimental properties such as product angular and translational energy distributions. The calculations well reproduced the experiments, and supported the assumption that the ozone complex formed by the two reactants overall does not live long enough to guarantee statistical energy redistribution among its degrees of freedom. The results were published in joint papers with the respective experimental groups [5,6].

2.2. We performed extensive studies on the reaction of H atoms with molecular oxygen in the triplet ground or the first excited singlet state, and compared the dynamics on the two potential energy surfaces (surface hopping was not considered). We have demonstrated that the electronic excitation of O_2 increases the rate of this chain-branching reaction by two orders of magnitude at flame temperatures. We have shown that the acceleration of the reaction is not connected to the extra energy pumped into the system by electronic excitation, but is the consequence of the difference in the topology of the potential energy surfaces. Namely, the reaction of the triplet O_2 molecules is exothermic, with no barrier to HO_2 complex formation from either the reactant or product side; that of singlet oxygen shares the same exit channels, is exothermic, but there is a barrier to complex formation. The latter is lower than the endothermicity of the reaction of triplet oxygen. With the calculations we revealed a misinterpretation of the experimental results, yielding an order of magnitude error in the rate coefficient used earlier in flame simulation. Our calculated rate coefficients have been utilized in new flame modeling, and allowed agreement with flame propagation rate measurements. We observed common features in the dynamics of both reactions. Based on the calculated information on the stereodynamics of the reactions, we identified which properties of the potential energy surface determine the overall reactivity. The results were published in the Journal of Physical Chemistry A. [7,8]

2.3. In collaboration with the experimental reaction kinetics group of Matthias Olzmann in Karlsruhe, we determined the mechanism of the thermal decomposition of the NCN radical, the reverse of the addition reaction of a C atom and an N_2 molecule. Based on earlier data from electronic structure calculations in the literature, the linear NCN was thought to isomerize to NNC, the decomposition of which would require surpassing a high barrier at a bent geometry. This picture did not explain the experimental findings. Investigating the ground and excited-state potential surface, we demonstrated that the decomposition can take place on the triplet potential surface, because the collinear NN-C arrangement allows barrier-less dissociation. This model lead to rate coefficients that match all experimental results. This work resulted in a joint publication [9]

2.4. We studied light emission that can be observed when singlet excited O_2 molecules in either gas- or liquid phase are produced in large concentration. This so-called dimol emission was assigned to formation of a weakly bound a van der Waals complex by two electronically excited O_2 molecules. Péter Szalay and Attila Tajti of Eötvös University performed very accurate ab initio calculations on the system, and found that the probability of light emission from the very weakly bound complex is rather small. In addition, the concentration of the complex at room temperature would be very low. We demonstrated that the characteristic red emission with energy twice as large as the singlet-triplet gap of molecular oxygen is collision-induced. It is made possible by the fact that when two singlet oxygen molecules collide, the collision energy (which is too high to allow the complex to stay in a bound state) allows them so close approach that the interaction borrows some transition moment to the spin-forbidden of light emission. We reported the results in J. Phys. Chem. Letters [10].

2.5. We performed extensive QCT calculations on the dynamics of the reaction of CH_3 radicals with HBr molecules. The reactants form a weakly bound van der Waals complex. We calculated the rate coefficient of the reaction starting from various quantum states of the reactants using a potential surface calculated and fitted by our collaborator Gábor Czakó. We obtained inconsistent results from which we concluded that the fitted potential surface incorrectly describe the entrance to the van der Waals well. We calculated 4000 additional ab initio points which, together with the points from the original calculation, were used to re-fit the potential surface (by our collaborator). The rate coefficient obtained on the corrected potential energy surface is characterized by a negative temperature dependence, in other words, the activation energy at low temperatures is negative. The QCT calculations yielded thermal rate coefficients in very good agreement with one group of experiments. The activation energy was found to be negative at low and positive at high temperatures. Rotational activation was shown to be responsible for the change of sign. Rotationally unexcited HBr radicals react with CH_3 with increasing cross section when the collision energy decreases, and the corresponding state-resolved rate coefficients increase fast when the temperature is reduced. Rotationally excited HBr (or CH_3) reactants are less reactive at low and more reactive at high collision energies, and the rate coefficient increases with increasing temperature. The minimum curve traced by the thermal rate coefficient arises from the balance of the contributions of reactants with low and high rotational excitation, respectively. At low and at high temperatures the majority of molecules are in low and high rotational states, respectively. In both temperature ranges the temperature dependence of the rate coefficient of the reaction of the more populated state dominates that of the thermal average rate coefficient, i.e. negative and positive dependence at low and high temperatures, respectively. The results are under organization for publication. The calculations are continued, this time on the collisions of the weakly bound van der Waals complex with rare gas atoms.

2.6. The reaction of the OH radical with HBr is governed by a potential energy surface similar to that of the CH_3 + HBr reaction. We used a fitted potential surface is available from the literature surface to derive thermal rate coefficients using the QCT method. The qualitative observations are the same as for CH_3 + HBr collisions. This reaction offered the possibility of using the Ring Polymer Molecular Dynamics method to calculate rate coefficients, accurately including quantum effects: both tunneling and the quantized nature of reactant vibration as well as rotation. In collaboration with Y. Suleymanov (The Ciprus Institute and MIT), we started to calculations with this method on the OH + HBr system. So far we concluded that the method works well at high temperatures, the numerical stability is poor at sub-room temperatures, so that either the technology or the accuracy of the potential energy surface function of the system has to be improved. From the high-temperature QCT calculations we obtained rate coefficient agreeing well with experimental results at room temperature and slightly above it, so that we used the theoretical data as extrapolation of the experimental ones. Together with similar dat for the CH_3 + HBr reaction, we published the results in a paper devoted to suggest high-temperature rate coefficients for modeling flame retardation by bromine-containing fire suppressants, where both reactions are important steps [11].

2.7. In order to support the photochemistry experiments in our institute addressing platform compounds derived from biomass, we studied the reaction involving ketyl radicals of aliphatic alcohols with triplet furfural and with 5-hidroxymethyl-furfural, where the reactants can form a van der Waals complex, and there are complexes produced by radical addition to the aromatic ring. We calculated the barrier heights for different addition channels as well as the structures of some possible products of the reaction to help the experimentalists identifying them. We also identified some tendencies in substituent effects in order to understand the factors governing the reactivity of cyclic triplet aldehydes. This work is still in progress.

2.8. Two isomer addition complexes are formed in the reaction of methyl-allyl radicals reacting with triplet molecular oxygen. The reaction has been studied experiments at the University of Helsinki. In order to perform the related theoretical modeling, Timo Pekkanen PhD student visited our group and spent one and half months in Budapest. We performed high/level ab initio calculations, and concluded that they are not accurate enough to decide whether the two addition processes, one at the chain-terminus and one at carbon No.3 take place without a barrier. We used the calculated data as starting points and varied the barrier heights in master equation simulations of the competition of reaction and collisional energy transfer, until we obtained values with which all available experimental data are reproduced.

The low-temperature rate coefficients proved to be characterized by negative, the high-temperature ones by positive activation energy. The results have been presented as a prestigious talk at the 37th International Symposium on Combustion, and appeared in the Proceedings of the Combustion Institute, the highest-impact journal of the field [12].

3. Complex formation in host-guest and transition metal – ligand systems

In these studies our role was to provide structural information and explanations to experimental observations.

3.1. In collaboration with the experimentalists group of Rita Skodáné Földes at the University of Pannonia, we investigated the formation of complexes of urea derivatives that are devoted to be appropriate for molecular recognition of 2,6-diaminopyridine. We investigated complexes that involve two or three hydrogen bonds and identified their structures to support the interpretation of NMR spectra. The joint paper has appeared in Organometallics [13].

3.2. In collaboration with the group led by József Bakos and Gergely Farkes at the University of Pannonia, chelate complexes of Pd, appropriate for stereoselective catalysis were studied. The ligands are open-chain pentane-2,4-diyl based aminoalkyl phosphines, with two chiral carbon atoms and a N atom which becomes chiral upon complex formation. The position of the methyl substituents induces stereoselective formation of chelates with a six-membered ring, in which the alkyl substituent of the coordinating N atom is either axial or equatorial. This group is close enough to the metal center, and by controlling its position, one can influence the possible directions of approach of a reactant in a catalyzed reaction. This way both stereoelectronic (due to the difference of the Lewis-base donor atoms, P and N) and steric effects can be controlled. The molecular geometries and relative energies of the possible conformers of numerous have been calculated using density functional theory, and the data were used in the interpretation of NMR spectra. In our latest work, the experiments and the calculations have been extended to S,N (aminoalkyl-sulfide) ligands and their complexes. The results have been published in the form of four papers [14-17].

3.3. In collaboration with experimentalists from our institute, we studied the possible intermediates of metathesis of dienes on Hoveyda-Grubbs 2nd-generation catalysts, and excluded the assumed deactivation of the catalyst by axial coordination of the diene to the catalyst that would block the active site from coordinating the second reactant. A joint paper has been published [18].

Coworkers participating in the project

István Mayer participated in the attempts to develop a new method for the description of weakly bound complexes. Tamás Rozgonyi and Ákos Bencsura helped in deriving formulas and in program development, respectively.

One postdoctoral fellow (Tibor Nagy) was employed for about 2.5 years from the funding. He was involved in the method development and data analysis in subproject 1.1-1.3, and gave three talks abroad at conferences. Subprojects 1.1-1.3 formed the basis of the PhD thesis of one of the two PhD students working on he project, Anna Vikár. Her thesis is under review. She presented posters at two international conferences and gave two talks at two meetings of the Reaction Kinetics Working Committee (RKFMB). The thesis of the other PhD student, Péter Szabó was written about the results listed as subproject 2.2, and was successfully defended in early 2017. In addition, subproject 2.5 and parts of subproject 2.6 were also performed by him. He gave two talks and presented two posters at two international conferences, and three talks at RKFMB meetings and at seminars. Both previous PhD students got jobs in scientific research, Péter Szabó in Sweden, Anna Vikár in an experimentalist group in the Research Ctr. for Natural Sciences, Budapest. BSc, later MSc student Szabolcs Góger worked on subprojects 2.6 and 2.7, and wrote four TDK papers on different aspects of the results; with one of which he won third place at the National Conference. He gave three talks abroad. Katalin Böőr as a BSc student participated in studies of complex formation, which was the subject of a TDK paper and her BSc thesis. József Király BSc student wrote the computer code on collisional energy transfer involving van der Waals complexes, and presented it as a TDK paper. Recent MSc student Katalin Szántó and BSc student Benjámin Csorba started working on different aspects of subproject 2.5.

The PI gave three invited and three regular talks at conferences abroad, lectures at two international schools, and presented some four posters at international conferences.
We participated in international collaboration involving three groups from the USA, one group from each of Taiwan, Germany, Ciprus, and Finland, and worked together with three groups from Hungarian universities.

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