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Reaction Kinetics: An Addiction

What is it that makes reaction kinetics so captivating that one can spend more than 40 years in this field? My first acquaintance with science was from an entirely different direction. I was born in 1940 in the small and traditional German university town of Göttingen where my father and grandfather were school teachers and at a time when teachers were often scientists, particularly good in local natural history. As a boy, my excursions with them and their colleagues provided stimulating encouragement to collect plants, fossils, and minerals. This early activity was the source of my great love for nature and, besides the attractions of treasure hunting and outdoor activity, it was not only fun but also an excellent introduction into careful observation and systematic approach to natural phenomena. Growing up in Göttingen was wonderful, in spite of both war-time and poor conditions afterwards. My grandfather was an ardent admirer of the great men of chemistry, physics, and mathematics who lived in Göttingen during his lifetime. He knew an endless number of anecdotes about David Hilbert, Walther Nernst, Max Born, James Franck, and all the others, and he never got tired of telling them over and over again. My father had a Ph.D. in medieval history, which added an older historical perspective. I was, of course, sent to the humanistic type of German “Gymnasium”, learning Greek and Latin, little English and French, but acquiring a solid basis in mathematics. The parents of several of my school friends were university professors: among them was Werner Heisenberg whom we all admired as the father who could recite Plato over lunch. He was not particularly amused when we ignited mixtures of sodium chlorate, a then common herbicide, and sugar in his basement among his wife’s clean washing, but otherwise “he was ok”. By the end of my school days in 1959, I was quite competent in botanic taxonomy and had a large collection of minerals, sometimes acquired under scary conditions being alone in quarries and mines, but somehow I got tired of it. Fortunately, at school my teacher of mathematics and physics had opened new vistas. Before the war he had worked as a physicist and, being unable to continue after the war, he became a teacher. The clarity of his presentations, the joy of making models and submitting them to scrutiny tests appealed so much to me that I abandoned botany and mineralogy, telling myself I would learn physics first and come back later to my old loves. One principle of this teacher which was instilled deeply in me was to always concentrate first on the essential before treating the side aspects: a healthy concept for many circumstances in life.

When I entered Göttingen University as a student in 1959, I was already familiar with this place of learning. Wilhelm Jost, the father of one of my school friends, had made his son and myself contribute in a playful but very educative way to his textbook on physical chemistry, by drawing figures and solving numerical problems. This remarkable man became my own scientific advisor, if not my scientific father. He was a truly humanistic scholar with the broadest cultural interests. Having been under his guidance, there was no doubt that I would also go into physical chemistry, starting from a solid education in physics and mathematics and then entering chemistry. My parents could not afford to let me study too long elsewhere, so after the first years at Göttingen, I spent just one year at the University of Freiburg and then returned to Göttingen in 1962. In order to learn English, Jost had recommended reading and translating N. B. Slater’s *Theory of Unimolecular Reactions*. I don’t remember where I got stuck, but at least the first 40 pages were an optimum introduction into what became one of my favourite interests later on. My first steps into laboratory under the demanding and most stimulating guidance of Heinz Georg Wagner were studies with shock waves. Jost and Wagner let me choose one of two topics for a diploma thesis: the shock wave induced dissociation of nitrous oxide or that of formaldehyde. Thank heaven I took the former, because only nowadays have we started to understand the latter. Shock wave studies in the early 1960s were less technically perfect than today. I remember sending a shock wave into a McLeod manometer, dispersing one litre of mercury over the laboratory and myself, which meant one month’s cleaning up. My companion Hans Alexander Olschewski and myself were really brave when running shock waves at several hundred bar. We took all conceivable risks: one complete laboratory was destroyed by fire from the hydrogen driving gas. Fortunately, missions of this type are not acceptable anymore. But we got there; we almost reached the high pressure regions of the unimolecular dissociations of molecules such as nitrous oxide, carbon dioxide, and carbon disulfide. The accompanying theoretical questions were quite appropriate for a physicist, unimolecular rate theory being built on simple statistical models, linking spectroscopic and molecular properties with macroscopically observable rates. RRKM and transition state theory were already well established and ready for use. Reaction kinetics started to develop its lure, being able to provide a continuous link from elementary molecular physics to complex phenomena like flames and detonations, asking for experiments with complicated but not too demanding equipment and leading to seemingly elementary and understandable chemical processes.

Having finished my Ph.D. thesis in 1965, Jost and Wagner in 1966 sent me to the U.S. on a three month visiting tour, starting at the Combustion Symposium at Berkeley where I first saw Harold Johnston, whose bond energy−bond order method had impressed me; continuing to stay for one month with Joe Hirschfelder at Madison, and ending at La Jolla to be with Kurt Shuler on his sabbatical. One would not call this a postdoctoral leave today, but it enabled me to meet many people like Raphy Levine and Dick Bernstein at Madison and, last but not least, Kent Wilson at La Jolla who introduced me, without much success, to surfing. Most importantly this short stay gave me the time and leisure to dream, to think, and to sort out my youthful thoughts. It bothered me that unimolecular rate theory at low pressures treated collisional energy transfer fairly carelessly in spite of the fact that it was the rate determining step. At La Jolla’s beautiful beach I managed to derive an analytical solution of the steady-state master equation for low pressure unimolecular reactions governed by collisions with exponential transition probabilities. This solution stood the test of time and still today provides a convenient link between bath gas collision efficiencies and average energies transferred per collision. My approach had much in common with Keck and Carrier’s treatment of diatomic dissociations and Evgueni Nikitin’s diffusion theory of rate constants, all being in the air in the mid sixties, my contribution just being tailored to the unimolecular reactions that we had studied in laboratory.

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After a series of experimental and theoretical studies of thermal dissociation reactions, I stumbled onto internal conversion processes as a way of selectively exciting unimolecularly reacting molecules in their electronic ground state. Laser technology was not yet advanced enough to allow for ultrafast time resolution, but collisions in high pressure gases could be used as a “poor man’s clock”, employing pressures in the hundred bar range which could provide a semiquantitative access to picosecond lifetimes of dissociating molecules. In a miraculous way, the quantum yield of the photolysis of nitrogen dioxide could be analyzed with respect to secondary bimolecular and termolecular processes and, at the same time, provide access to the primary bond breaking. The derived energy-specific rate constants for the latter process were of the correct magnitude such as confirmed in time-resolved laser picosecond experiments three decades later by Curt Wittig and his co-workers. All that had been needed for my early experiments was a steel tube with thick glass windows, a lamp, a filter, a photomultiplier, and a recorder. Never again was I lucky enough to do a key experiment with such little equipment.

Wilhelm Jost and Heinz Georg Wagner had pushed me to write a habilitation thesis in 1967 which, in my late twenties, brought me onto the market of applying for professorships. In 1970, I was offered a physical chemistry chair at the young Ecole Polytechnique Fédérale de Lausanne (EPFL). A transformed wooden Swiss army hut became my laboratory and my office from 1971 on. It looked ridiculous but was located in a most beautiful park on the shore of Lake Geneva. Tino Gäumann from the EPFL had spotted me as a promising youngster, invited me, and negotiated the offer in a single day. What else could I do than accept after only a few days of hesitation? Looking back and comparing this with today’s agonizing hiring procedures it was almost like a dream. Likewise, being able to import a complete crew of first-rate companions like Klaus Luther, Horst Hippler, and soon afterwards Martin Quack, who all then did their Ph.D. at Lausanne, was a gift hard to match. The group increased in size, in spite of the minimum laboratory and office space in our two army huts. We built a shock wave laboratory, set up a laser laboratory, and continued high pressure steady-state photolysis experiments up to a kilobar. What a stimulating period! Laser flash photolysis experiments allowed us to follow atom recombination from termolecular to diffusion-controlled behaviour. Laser flash photolysis also permitted an access to photolytic cage effects in medium to high pressure gases. Temperature dependences of continuum absorption spectra in the UV, such as studied in shock waves, developed into spectroscopic molecular thermometers with ultrafast time resolution. The high-temperature UV spectrum of HO_2 radicals, which I was the first to see in shock waves in 1968, was studied further and analyzed quantitatively. Being employed to teach thermodynamics and mathematics in French to chemists was the most efficient crash program in learning this beautiful language. And then there were the hikes and skiing days in the mountains: it was a wonderful time and it was not too difficult in 1974 to turn down the first offer to return to Germany, to the University of Würzburg.

After having read about the compound nucleus model in Blatt and Weisskopf’s *Theoretical Nuclear Physics*, Martin Quack and I went into one of our main themes in reaction kinetics, the elaboration of a statistical adiabatic channel model (SACM), its principle, and its simplified realization at a time when accurate adiabatic channel potentials on ab initio potential energy surfaces were difficult to obtain. Martin obviously was a born spectroscopist while I came from kinetics, which made us a good team. Like Ariadne’s thread, SACM has accompanied both of us over the next decades. Germany’s present chancellor, Angela Merkel, was fifteen years later one of the first to calculate adiabatic channel potentials on early ab initio potentials of the methyl radical. Who knows whether she still remembers SACM?

In 1975 another offer to return arrived from Germany, this time from my home town Göttingen, to become the successor of my old teacher Wilhelm Jost. How could I turn that down? However, it was a hard decision to leave the quickly developing EPFL and Tino Gäumann, who had provided such a generous welcome. The beauty of the Canton de Vaud, Lake Geneva, the Swiss Jura, and the Alps had become part of myself. Going back to Göttingen, therefore, was only possible after having bought a chalet not too far from the lake, in a large natural paradise at 1100 meter altitude. This chalet, over the years since, has become the home of the IUPAC task group of atmospheric kinetics, and the IUPAC data bases for atmospheric modelling have been elaborated here, in more than thirty working weeks. Contributing to the folklore of atmospheric chemistry by providing hospitality to a group of colleagues from this field has become a particular privilege.

The move from Lausanne to Göttingen brought about the change from a small group of young people working closely together, to a much larger scientific environment located in the university institute and in the Max-Planck-Institutes for Biophysical Chemistry and for Fluid Dynamics. The large group of first rate reaction kineticists, dynamicists, spectrocopists, photochemists, and quantum chemists, all being close, provided a great opportunity to develop collaboration in all parts of reaction kinetics. Jürgen Wolfrum, my old friend from early university days, was there, and driven by his restless energy we founded a local center of excellence, the Sonderforschungsbereich on “Photochemistry with Lasers”; it operated for 15 years, and after that another Sonderforschungsbereich on “Molecular Mechanisms of Unimolecular Processes,” which continued for 12 more years until 2004. As a consequence of the close collaboration with colleagues from other institutions, in 1990 I was invited to take over the section of spectroscopy within the Max-Planck-Institute of Biophysical Chemistry, becoming the successor of Albert Weller. Here I “inherited” a wonderful group of competent photochemists and enjoyed close collaboration with Albert until his death. At the same time, with Fritz Peter Schäfer from the same Max-Planck-Institute and Dirk Basting from the laser company Lambda Physik, we founded an independent research institute, the Göttingen Laboratory for Laser Technology (LLG).

Our local research centers were generously funded by the German Science Foundation (DFG) and allowed for the establishment of long-term research projects. One of them was based on the systematic exploitation of the spectroscopic molecular thermometers which we had derived from our shock wave studies by measuring the temperature dependences of UV absorption continua. The observation of Gaussian-type shapes of molecular absorption continua, their interpretation by reflecting oscillator wave functions on upper-state repulsive potential curves, and their broadening because of the excitation of vibrational states opened the door to a direct detection of excited-state dynamics. Having verified that the spectra of canonical and microcanonical ensembles were practically identical, absorption coefficients could be calibrated as a function of the energy by measuring their temperature dependences. In the hands of Klaus Luther and Horst Hippler, this permitted the time-resolved analysis of stepwise collisional deactivation of laser-excited molecules, after their initial electronic excitation by internal conversion had been converted into high vibrational excitation. In friendly competition with John Barker, "his" hot IR and "our" hot UV spectroscopies provided new and direct information on the step-sizes of intermolecular energy transfer. To our delight, the same molecular thermometers could be used also through the range of highly compressed gases into the liquid phase. After accounting for local density effects in binary collision numbers, Dirk Schwarzer much later then could even show that the step sizes remained practically unchanged from gas to liquid phase. Our work on intermolecular energy transfer at high excitation energies continues until today. Klaus Luther, Thomas Lenzer, and their co-workers with kinetically controlled selective ionization (KCSI) succeeded in revealing more details of the collisional transition probabilities; their functional form was indeed found to be close to exponential gap laws. However, deviations from this law could also be detected and their relevance for thermal unimolecular reactions investigated.

In another line of research with Klaus Luther and Horst Hippler, again hot UV absorption spectra could be exploited to study dynamic phenomena of vibrationally highly excited molecules, brought by light absorption and subsequent internal conversion into energy ranges where dissociation or isomerization takes place. The ability to spectroscopically distinguish these hot reactive molecules from cold unreactive molecules, permitted the time-resolved determination of energy-specific rate constants of unimolecular reactions. Since our first experiments about 25 years ago, much more detailed state-selection could be achieved, such as in Bernd Abel's *J*-selective measurements from our group and in work from many other laboratories. Experiments of this kind called for more detailed theories of unimolecular bond breaking processes, in potentials without barriers for the reverse bond formation. It was wonderful that Martin Quack, after his postdoctoral stay at Berkeley, came back to Göttingen for a number of years and the SACM approach to bond breaking processes could be developed into more rigorous implementations of the properties of potential energy surfaces. After Jörg Schroeder had joined our group, the study of cage effects and atom recombination rates of iodine and bromine in highly compressed gases and liquids was picked up again. Horst Hippler reached bath gas pressures up to 7 kilobar, which required special safety precautions. Instead of shielding the extended apparatus by thick walls, we put the experimentalist into a shelter made from steel. Such experiments were done with a lot of palpitations and thrills; the great competence of our workshop, however, guaranteed uneventful operations. The simple idea behind the high pressure measurements was our belief that kinetics in liquid phase could be better understood if one approached this medium slowly by gradual increase of the solvent density from the side of the gas phase. A large number of studies of this type made reactions in supercritical fluids one of our favourite research topics.

With the arrival of laser picosecond spectroscopy, fast reactions in supercritical and liquid environments became accessible more easily. Of course, like many others, we became attracted to the photoisomerization of stilbene. This molecule apparently is highly infectious; once one has touched it, one cannot get away from it. Jörg Schroeder devoted great effort to the study of this photoisomerization reaction and its transition from gas to liquid phase behaviour. We always saw it in comparison to the photoisomerization of diphenylbutadiene and we are still puzzled by the markedly different properties of the gas–liquid transition of these two photoisomerization systems. Are there differences in the solvent modifications of the effective barriers or different types of solvent influences on intramolecular vibrational redistribution? Using our hot absorption molecular thermometer, Dirk Schwarzer was able to employ this technique in an ever more sophisticated way for studying time-resolved intramolecular energy flux. He synthesized molecules with two chromophores and observed the transport of vibrational energy from one hot chromophore through a bridge to a second cold chromophore. At the same time the intermolecular energy loss into the surrounding liquid environment was followed. Extensive molecular dynamics modelling by Jörg Schroeder and Dirk Schwarzer of the intra- and intermolecular dynamics provided the theoretical analysis and taught me that there are limitations to my obsession to cast everything into simple models. Maybe I had too often read the motto "simplex sigillum veri" on the wall of the Göttingen physics lecture hall of my student days.

The large attraction of reaction kinetics not only lies in its beautiful link of elementary phenomena with practical applications, but also the intense family life of the community, in combustion, atmospheric chemistry, gas kinetics and so on, bringing together experimentalists, modellers, users, and theoreticians. Having grown up with RRKM theory of unimolecular reactions on the one hand, measuring falloff curves and seeing the application in the kinetics community on the other hand, I became irritated very early on the lack of simplifying models on an intermediate level. During one of his sabbatical stays at Göttingen, in 1978, I complained about this to Fred Kaufman. Fred simply asked me, "Why don't you try to do better?" What emerged from this challenge was my simplified reduced representation of falloff curves which I considered annoyingly primitive but which found its way into many people's data representations. Remembering what I was taught at school, I started preaching that one cannot understand falloff curves if one does not understand the low and high pressure limits. The range in between is almost only interpolation. I had started representing the low pressure rate constants in a factorized way, separating the well-known from the less well-known contributions. This factorizing method is still in use, telling where our largest lack of knowledge continues to be. The search for high pressure rate constants at first showed that there existed very few experiments at pressures above 1 bar. Therefore, with Klaus Luther, Horst Hippler, and many younger co-workers we tried and are still trying to reduce that lack of data. Here, reaction kinetics again demonstrates its attractive facets: high pressure rate constants provide access to the otherwise difficult accessible region of the potential where reactions take place. Having measured many high pressure rate constants, a quantitative understanding was asked for and SACM again became our tool. However, unlike the simplified adiabatic channel interpolation schemes of early SACM, now real potentials and accurate eigenvalue calculations along minimum energy paths were required. Larry Harding from Argonne provided us with suitable ab initio potentials for key systems such as NO_2 or HO_2, other potentials were constructed on the basis of their limiting properties. It was more than fortunate that Evgueni Nikitin in the late 1980s was again allowed to leave Moscow and that he brought Anatoli Maergoiz and Vladimir Ushakov to Göttingen. Together with them, systematic calculations of eigenvalues along reaction coordinates, the adiabatic channel potential curves, were made, extending Martin Quack's simple eigenvalue interpolations from the early 1970s. In addition, when too many channels became important, which was considered a serious obstacle to practical applications of SACM, classical trajectory (CT) calculations took the place of the channels. As a consequence, SACM/CT today is our method of choice for treating bond fission/bond formation processes. The results are often similar to the early simplified SACM or to microcanonical, flexible variational transition state theory. However, “dynamical corrections” such as “recrossing” are not required and the transition between the adiabatic and nonadiabatic limits of the dynamics is adequately represented. The approach allows also for the implementation of quantum effects on a much less time-consuming level than is done in complete quantum scattering calculations. And again one follows the complete route from first principle treatments of elementary processes to rate constants and to the modelling of large mechanisms for practical use. The temptation is great to apply the tools to an ever increasing number of fields, such as high temperature ion−molecule reactions in my recent collaboration with Al Viggiano, to low temperature ion−molecule reactions in projects with Bertrand Rowe, to ultralow temperature kinetics together with Evgueni Nikitin and their co-workers. I close this report with my guess that an addiction to reaction kinetics cannot be cured. At least this applies to me.

Jürgen Troe