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Conference Report

FOURTH INTERNATIONAL CONFERENCE ON CHEMICAL KINETICS Gaithersburg, MD July 14-18, 1997

Report prepared by

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1. Introduction

This was the fourth in a series of quadrennial conferences designed to bring together scientists from different areas who have a common interest in chemical kinetics, both in the gas and liquid phases. These scientists include both those who generate and those who use chemical kinetic data. This utilization of chemical kinetics is predominantly in the modeling of complex chemical processes. The importance of chemical kinetic data in modeling the atmosphere has been apparent for some time now; indeed without reliable kinetic rate constants, it would not be possible to understand, and indeed now to predict, the effects of halogen-containing compounds on the earth's stratosphere. This understanding led to the phase-out of chlorofluorocarbon and bromofluorocarbon production, in spite of the industrial importance of these compounds. The reaction kinetics of chemical transformations in the troposphere is also a key part of widely used models of photochemical smog formation. These data also are utilized in regulatory processes and, thus, the reliability of the chemical kinetics underlying them is of considerable importance.

The application of the kinetics of elementary reactions to atmospheric chemistry is quite well known, even outside the scientific community. Less well known is the application of chemical kinetics data in modeling combustion systems and industrial processes in order to bring about improvements in efficiency and to minimize toxic emissions. This use is likely to increase in importance as concerns about global warming lead to increased interest in energy efficiency and as environmental concerns place additional constraints on the release of harmful process by-products.

Chemical kinetics is also playing an increasing role in physiological chemistry. Here, the deleterious effects of free-radical oxidants is a major concern and the evaluation of these effects, and the impact of antioxidants, requires information on the reactivity of these radicals towards physiological constituents. Further, disease treatment, particularly cancer therapy, often relies on free radical generation. The importance of small free radicals was highlighted by the naming of nitric oxide as "molecule of the year" by *Science* magazine.

The Fourth International Conference on Chemical Kinetics was designed not to focus specifically on a single problem to which chemical kinetics is applied. Rather, the goal was to have a much wider ranging conference where practitioners and users of chemical kinetics would be exposed to more diverse information, so that they could draw upon much more of the wealth of the field.

The conference was supported by the National Institute of Standards and Technology, the National Aeronautics and Space Administration, and the NIST Office of Standard Reference Data. Two hundred scientists attended the conference, including representatives from 21 countries. The delegates heard 57 oral presentations, which included 4 invited lectures. Also, there were 140 poster presentations.

The Conference was also served by a World-Wide-Web site, through which conferees could obtain information about the conference, register, transfer to the web site for the meeting hotel or other hotels in the area, etc. All abstracts for the meeting were posted on the web site and were available to all of the conferees well in advance of the conference. The file of conference abstracts could be searched by key word or by author, and an Acrobat file was also available for downloading. This web site will remain active for 1 year after the end of the conference at: http://www.nist.gov/cstl/div838/kinet_conf/conference.html. The oral sessions were grouped about specific themes. The poster sessions did not focus upon specific themes; instead, each was designed to reflect as much as possible the entire oral program. Their diffuse distribution enabled better communication among specialties. To aid the attendees, the web site also had links from the oral sessions to topical posters, which served to integrate better the poster presentations with the oral program.

2. Proceedings

The conference opened with the first of three sessions on small radical kinetics, chaired by Robert Huie of NIST. The opening talk, by Sidney Benson of the University of Southern California, set the stage for some spirited discussion on the kinetic parameters for direct metathesis reactions, reactions in which an atom is transferred. This discussion involving both this and other papers in the session. The intense interest in these parameters arises from their use in determining thermodynamic properties for these free radicals. These quantities are far from agreed upon. After the morning break, E. T. Denisov of the Institute of Chemical Physics of the Russian Academy of Sciences in Chernogolovka delivered the first invited lecture, in which he discussed the semiempirical methods he has developed for determining kinetic parameters for addition and abstraction reactions for free radicals utilizing a model based on the crossing of two parabolic potential energy curves. This was followed by more papers on the experimental determination of these parameters for small free radicals.

The afternoon session, chaired by Jeffrey Manion of NIST, focused on high temperature reactions of inorganic free radicals. These reactions are often key to combustion processes and the formation and removal of pollutants in combustion systems. A considerable amount of detail on these reactions is being elucidated. This was particularly apparent in a discussion of the $H + O_2$ reaction, where 15 vibrational states of O_2 were considered explicitly.

The Tuesday morning session, chaired by Wing Tsang of NIST, highlighted reactions of unsaturated organic radicals. Many of these reactions are thought to be key intermediate steps in the formation of fine particulate matter in combustion systems, and are thus of particular importance in light of the possible changes in air particulate standards. After the morning break, M. C. Lin of Emory University presented an invited lecture on the kinetics and mechanisms of phenyl radical reactions, as investigated by three complementary experimental techniques.

The Tuesday afternoon session, chaired by Anthony M. Dean of Exxon Research and Engineering Company, was titled Theory and featured papers which were primarily theoretical. An important feature of the entire Conference, however, was the extent to which the application of theory to kinetic problems pervaded the discussion. A large portion of the papers described as experimental had some theoretical component, often serving as an important guide to the interpretation of the experimental results. Further, the theory papers were clearly closely coupled to experimental work and to developing tools which can be more readily applied as practical adjuncts to experiment.

On Wednesday morning, a session on solution kinetics was held, chaired by Pedastur Neta of NIST. Papers included not only investigations in classical solutions, but also a study in supercritical water and an investigation of the use of the modulation of radical kinetics by electric or magnetic fields. After the break, a session on low temperature studies, chaired by Tomas Baer of the University of North Carolina, started with an invited talk by Mark A. Smith of the University of Arizona on the application of supersonic flow techniques to ion and radical kinetics at the low temperatures created by the expansion. The afternoon session, chaired by Jürgen Troe of the University of Göttingen, was the second on small radical kinetics. The range of topics covered illustrated well how the understanding of the reactions of small free radicals is important to many applied areas of chemistry. Further, it illustrated the close tie that has developed between theory and experiment. The applications covered ranged from modeling the effects of chlorine on stratospheric ozone, through new explosives and propellants, to hydrocarbon combustion chemistry.

On Wednesday evening, the conference banquet was held, featuring a speech by Sidney Benson of the University of Southern California. Dr. Benson's textbook, *The Foundations of Chemical Kinetics*, published in 1960, is recognized as one of the cornerstones of modern chemical kinetics. Subsequent papers, and the book *Thermochemical Kinetics,* laid the foundation for the application of group additivity in chemical kinetics and in free radical thermodynamics. Dr. Benson gave an enlightening, entertaining, account of some of the early work in free radical chemistry, prior to the explosion in activity which started in the 1960s and continues to the present day, as evidenced by the papers in this conference.

Thursday morning started with a session on applied kinetics, chaired by Joseph Durant of Sandia National Laboratory. This session was designed to represent more directly some of the applications of chemical kinetics to industrial problems. Of course, the applications of chemical kinetics to real problems was pervasive throughout the meeting, but the papers presented here tended to emphasize more heavily the industrial setting. The afternoon session was on heterogeneous chemistry and was chaired by Michael Kurylo of NIST. This field of chemistry has grown tremendously in the past few years, due to the recognition that heterogenous processes can play an important role in atmospheric chemistry. An invited talk on the subject of atmospheric chemistry and photochemistry on ices was given by John R. Sodeau of the University of East Anglia.

The final session of the conference on Friday was also the third session devoted to small free radical kinetics. This session was chaired by Jeffrey W. Hudgens of NIST. These papers again illustrated the relationship among basic kinetic studies, theory, and application to practical problems. They also demonstrate how well the details of complex systems are becoming understood by the combination of theory and experiment.

Poster sessions were held on Monday, Tuesday, and Thursday afternoons at the Gaithersburg Hilton. Due in part to the linkages set up in advance between the poster presentations and the thematic oral sessions, the poster sessions proved to be very successful, with spirited discussion continuing into the evening.

3. Conclusion

This conference has continued to serve its stated function of bringing together scientists who generate kinetic data and those who make use of these data. An additional function which has evolved is to demonstrate the application of theory to kinetic problems. This conference is now a major venue for this exchange and we expect this role to grow in the future. Underlying all of the presentations were the applications of kinetic information to practical problems, ranging from modeling the stratosphere to modeling industrial processes.

The utilization of the World-Wide-Web for the conference proved to be very successful. Numerous compliments from the participants indicated the usefulness of having the abstracts available in advance of the meeting. Indeed, the counter on the web site indicated heavy usage. The use of the web also allowed better integration of the oral and the poster sessions, a problem often encountered in meetings such as this. This was done by linking relevant poster abstracts to specific oral sessions. Participants were able to check these abstracts in advance of the meeting and select the specific posters to visit. The abstracts could also be searched by key words, again allowing the participants to have adequate information in advance of the conference. Future uses of the web will undoubtably be even more extensive. Indeed, we anticipate that in subsequent conferences, we will allow longer and more complex abstracts, with color illustrations encouraged, for publication on the web site, whereas abstracts for the abstract book will probably be more limited.