

CHEMICAL KINETICS— THEORY AND EXPERIMENT

The International Conference on Chemical Kinetics held June 17–19, 1985 at the National Bureau of Standards in Gaithersburg, MD, was attended by about 200 scientists from academic, industrial, and government laboratories. The meeting was sponsored by the Air Force Office of Scientific Research, the Environmental Protection Agency, the Gas Research Institute, the National Aeronautics and Space Administration, the NBS Office of Standard Reference Data and the Center for Chemical Physics, and the National Science Foundation. The purpose of the conference was to bring together investigators from a broad range of institutions and backgrounds to review progress and problems in theoretical and experimental chemical kinetics.

The conference in many ways was a continuation of the highly successful symposium held at NBS seven years ago under the chairmanship of Prof. Frederick Kaufman, entitled "Current Status of the Kinetics of Elementary Gas Reactions: Predictive Power of Theory and Accuracy of Measurement." Its scope was considerably broader, however, in that in addition to gas phase phenomena, the program included sections on ionic reactions and reactions in the condensed phase. This is indicative of the exciting developments in chemical kinetics in recent years. The exploitation of new experimental techniques and a deeper theoretical understanding have led to a confluence of the many individual elements in formerly diverse areas of chemical kinetics so that it is now possible to think in terms of the commonality of problems.

The meeting, which was chaired by John T. Herron, consisted of six half-day sessions. The first was held in honor of Prof. Sidney W. Benson for his many outstanding contributions to chemical kinetics. It involved a number of technical contributions by his colleagues. These included H. E. O'Neal, Robin Walsh, A. J. Colussi, S. E. Stein, and K. D. King, along with a presentation by Prof. Benson himself. The session was chaired by R. Srinivasan and was introduced by D. Golden.

Subsequent sessions covered Fundamentals, chaired by R. M. Noyes; Unimolecular Reactions, chaired by M. Bowers; Energy Transfer, chaired by S. H. Bauer; Reactions in the Liquid Phase, chaired by C. Walling; and Bimolecular Reactions, chaired by M. Pilling. Each session began with a series of 30-minute invited talks. This was followed by a 75-minute coffee break where the posters of papers pertain-

ing to that session could be examined, and then an hour discussion session led by the chairman and the invited speakers. The invited speakers and their topics were as follows:

H. F. Schaefer III, "The F+H₂ Potential Energy Surface. The Ecstasy and the Agony"; J. Troe, "Elementary Reactions in Compressed Gases and Liquids: From Collisional Energy Transfer to Diffusion Control"; E. M. Arnett, "Comparison of Thermodynamics and Kinetics for Some Important Bond-Making and -Breaking Processes in Organic Chemistry"; W. L. Hase, "Unimolecular and Intramolecular Dynamics. Relationship to Potential Energy Properties"; Thomas Baer, "The Dissociation Dynamics of Energy Selected Ions"; J. J. Gajewski, "Empirical Approach to Substituent Rate Effects in [3,3]-Sigmatropic Shifts Utilizing the Thermochemistry of Coupled Nonconcerted Alternative Paths."; H. M. Frey, "Energy Transfer"; J. R. Barker, "Large Molecule Energy Transfer: New Techniques and New Controversies"; J. C. Stephenson, "Vibrational Relaxation of Chemical Bonds in Liquids and on Surfaces"; J. I. Brauman, "Prediction of Rate Constants for Ionic Reactions in the Gas Phase and in Solution"; J. A. Howard, "Measurement of Absolute Propagation and Termination Rate Constants for Alkylperoxyls in Solution by the Hydroperoxide Method"; J. H. Espenson, "Kinetics and Mechanisms of Inorganic Reactions in Aqueous Solutions: Intermediates"; T. H. Dunning, Jr., "Theoretical Characterization and Calculation of Potential Energy Surfaces for Chemical Reactions"; and J. Wolfrum, "Laser Stimulation and Observation of Bimolecular Reactions."

Prof. Frederick Kaufman was scheduled to give a talk entitled "Kinetics of Bimolecular Processes" but was unable to attend the meeting because of an illness that was to prove fatal. His loss removes not only one of the world's leading figures in gas kinetics but a man deeply admired for his wit, dedication, and humanity.

The titles of the talks give a clear indication of the scope of the conference. The hour-long discussion periods concluding each session were especially valuable. Under the direction of the chairman, and with the invited lecturers providing guidance, the discussion provided an in-depth look at the current state of each area.

A special feature of this meeting was the bringing together of kineticists from many disparate areas of chemistry.

In all these areas, modern techniques allow us to focus on the fundamental interactions. At this level, the commonality of the effects are clear and we can all learn a great deal from each other. The new methodologies and broadened theoretical understanding have led to two distinct directions in experimental work: the study of truly fundamental processes in the form of state-to-state chemistry, and the study of thermal reactions involving molecules of increasing complexity.

To be truly meaningful, all such studies must be firmly wedded to theory. In the case of state-to-state studies, it appears that the experiments are considerably ahead of theory. It is thus extremely difficult to generalize about the many interesting observations. In the area of thermal reactions, semi-empirical approaches based on transition state theory, and within the framework of thermochemical kinetics, have proved to be an extremely useful concept in explaining observation and clearly will have an increasing predictive capability. Interestingly, it is in this area that theory may play an ever more important role. Thus, while *we may continue to have problems using theory to generate accurate potential energy surfaces or to describe motion on these surfaces*, the description of a molecule at the bottom of its well in terms of its energetics and energy, at least at a semi-empirical level, is approaching an accuracy that rivals direct measurement, at least for smaller molecules. Since this is a large fraction of the information that is needed for the application of transition state theory, one can foresee many exciting developments in the quantitative aspects of the chemical kinetics of thermal reactions.

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