

Reaction dynamics: concluding remarks

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The 157th Faraday Discussion represented a historic turning point in the development of the field of reaction dynamics because it concerned itself with how reactions occur in gases, in liquid, and at interfaces. Never before has the attempt been made to unify the various approaches to reaction dynamics in one Faraday Discussion meeting and to discover what language was common and what was special to these previously distinct subdisciplines. This Discussion also marked a maturation of the field of reaction dynamics in that so much emphasis was placed on what the combination of theory and experiment could tell us about the detailed course of chemical transformations.

I Introduction

This is the first time that a Faraday Discussion had devoted itself to the topic of reaction dynamics in and between all different phases of matter – a brave decision by the organizers of this meeting, which rewarded the participants with many insights into previously unrealized interconnections. Professor F. Fleming Crim, University of Wisconsin, set the tone for this meeting with his superb Introductory Lecture¹ on chemical transformations across phases. This theme was continued by the many presentations and discussions found in this volume. It is not my purpose here to provide “a Readers Digest account” of what transpired. Instead, I offer some of my own perspectives on this field.

I begin by sharing with you a photograph (Fig. 1) I took in sun-drenched Italy in June, which reminds me of the superb location of our meeting in Assisi. In many ways this snapshot captures the field of reaction dynamics – obvious beauty to behold, but many features hidden from view, even behind barred passages. With advances in both experiment and theory the window is being lifted for us to view inside and the field of reaction dynamics is providing us with rich pictures of how chemical reactions do take place. We have come very far from the early times when chemists first started questing after the knowledge of chemical change, collision by collision, and yet so many questions remain unanswered. At the heart of chemistry are chemical transformations of all types and the understanding of how they happen continues to represent a central problem in all chemistry.

Often it is best to decide what comes next by reflecting on the past. The birth of reaction dynamics begins with the study of isolated gas-phase collisions, whether by infrared spectroscopy as pioneered by John Polanyi and co-workers or crossed molecular beams, pioneered by Dudley Herschbach and co-workers. Of course, there were many others who contributed to early ground-breaking experiments but the names of Polanyi and Herschbach stand out as icons in this field. We are so appreciative that John Polanyi could join us for this Discussion and share with us his new work on surface-controlled reactions.² We were also so fortunate that the President of the Faraday Society, Prof. Michael Ashfold, was also able to join us and add so much to our conference.

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Fig. 1 Flowers in a window, taken in Siena, Italy.

II Past, present and future

In the beginning, detection schemes were truly primitive. Isolated gas-phase collisions imply necessarily low concentrations of collision partners, which places a challenge on how the reaction products can be detected. We think back on what was called “the Alkali Age” in which only alkali-atom containing molecules could be probed, which was accomplished by means of hot-wire ionization. This was followed by the use of mass spectrometric detection, so powerfully demonstrated by Yuan T. Lee and co-workers among others. This technique provided universal detection of reaction products but was almost completely blind to the quantum state distribution of the products. This situation would dramatically change with the introduction of the laser, which not only provided quantum state resolution but could interrogate reactions on increasingly shorter time scales, today reaching to femtoseconds and attoseconds. Another remarkable development was ion imaging, pioneered by David Chandler and Paul Houston, and further developed by others such as André Eppink, David Parker, Arthur Suits, Hanna Reisler, and others. At the same time we should not forget what pulsed nozzle beams have made possible for studies of reaction dynamics, pioneered by John Fenn, Ronald Gentry, and others. As time-resolved spectroscopies have been developed and refined, the ability to study reactions in and across various phases of matter by “pump-probe techniques” has dramatically improved, beginning with gas-surface scattering, reactions in liquids, *etc.*

At the same time, theoretical approaches have deepened and reached the stage that every experimentalist must look to theory in helping to interpret reaction dynamics results. In the beginning, reaction dynamics was most successfully pictured by means of hard-sphere collisions, like some game of billiards. As we have seen during this Discussion, these ideas are still alive and well, and progress is also made by considering soft-sphere collisions, which allow energy transfer into the internal degrees of freedom of the reaction products. The most dramatic advances can be attributed to the generation of chemically accurate potential energy surfaces through advances in quantum chemistry, which owe so much to the ingenuity of theorists and the advances in computational power. We learn that in many chemical reactions we are not simply playing a straightforward game of billiards but the billiard table becomes warped as the billiard balls move on the table, which can easily confound some simple intuitive ideas. Most ground-state reactions are considered to occur on a single potential energy surface, but increasingly we realize that nonadiabatic effects cannot be ignored and can in certain cases, particularly in excited states of polyatomic systems through conical intersections, become dominant in controlling the outcome of reactive collisions. In that sense we are not simply playing billiards on a warped billiard table whose contours change in time but rather on interconnected billiard tables whose shapes change in time! In this regard the surface hopping approach pioneered by John Tully³ and its further elaborations as well as the *ab initio* multiple spawning method pioneered by Todd Martinez⁴ are of great interest and hold much promise. We have also been treated by Donald Truhlar to an exposition on a coupled-mode theory called multi-structural variational transition state theory, which includes a treatment of the differences in the multi-dimensional tunneling paths and how they contribute to the reaction rate.⁵

I cannot emphasize enough the power of the question in defining new directions for a field. At this Discussion speakers were kept on their toes by many probing questions, especially from Joel Bowman, David Glowacki, David Nesbitt, Daniel Neumark, and Donald Truhlar. We seek to know how atom-plus-diatom reactions differ from complex reactions involving polyatomic reagents having many degrees of freedom. This statement is particularly true when reagents are internally excited in different ways. We must not let ourselves become locked into imagining all reactions take place close to the minimum energy path or that reactions pass through some one point called simply the transition state. Past and present work on migratory insertion and what is called roaming has amply demonstrated the dangers of becoming intellectually phase-locked into too simple pictures of reaction dynamics that do not allow the possibility of gross rearrangements of the nuclei in the course of a reaction. We need to understand better the role of clusters and of solvents in mediating reaction dynamics. Environmental effects can be of major importance in determining reaction outcomes. We are learning so much from the careful study of vibrationally resolved small radical–molecule reactions and how they compare to the same reactions in the liquid phase, for example. The same is true for ion–molecule reactions.

We should not imagine that the same questions asked of a gas-phase reaction are necessarily what are important in describing reactions occurring in the condensed phase. In my estimation, the one word that most belongs to chemistry is the word ‘catalysis’. If I have a criticism, it would be that we did not hear enough about the reaction dynamics of catalytic systems, particularly biological catalysts called enzymes – but hopefully in the next such Discussion we will. Nevertheless, the topics covered in this meeting were amazing in their breadth, spanning elementary reactions to how crowding affects protein folding!

I do suggest we must keep in mind what we are seeking to uncover about nature. To some it is simply how well theory and experiment can be put into agreement. To me, this goal is certainly laudable but I seek more. I seek the ability to learn what features can be applied with some confidence in predicting and understanding the behavior of related but more complex reactions. I leave this meeting energized

with the conviction that reaction dynamics has a bright and healthy future. We owe a great debt of gratitude to the organizers, Piergiorgio Casavecchia, David Clary, Peter Hamm, Andrew Orr-Ewing, George Schatz, and Alec Wodtke, who put together a most memorable conference.

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