

## Seeing into chemical reactions

**Reaction Dynamics: Recent Advances.** N. Sathyamurthy, editor. Narosa, New Delhi, 1991. 203 pp. Rs 250. Also available from Springer, Berlin, DM 128.

The past decade has witnessed giant leaps in our knowledge of the dynamics of chemical reactions, and this is from efforts on both the theoretical and experimental fronts. In India also there has been a spurt in research in both directions, but more so in the theoretical side. This book is the outcome of two winter schools held at the Indian Institute of Technology (IIT) in Kanpur. Nearly all the authors are less than forty-five years old and five of them do not participate in any experimental effort. However, there is a good coverage of important experiments. Most of the experiments are highly sophisticated and very expensive, and the experimental effort in India is limited to a very few laboratories. Even in these the level of sophistication and versatility is far below those found in well-established laboratories dedicated to the study of reaction dynamics.

As this is an edited collection of articles, the scope of coverage varies from chapter to chapter, reflecting the interests and attitudes of the authors. Some can be considered as very good introductions to the general areas they purport to cover; a few others address themselves to very specific current problems in reaction dynamics and provide a good review of the current situation. Some are so terse and also limited in scope that they only serve to bring to our notice the importance of the subject under discussion.

Molecular beam scattering studies have been in vogue for several decades. The development of supersonic jets and beams have opened new vistas. The experimental techniques for the study of intermolecular forces through measurement of scattering cross-sections have been briefly, but adequately, described (P. K. Chakraborti). The results of some of the leading groups in the world (Göttingen, Berkeley, Irvine, Perugia, etc.) have been chosen as illustrative examples. The study of clusters, which bridge the gap between the gaseous state

and the condensed state: atoms/molecules  $\rightarrow$  clusters  $\rightarrow$  solid/liquid, has advanced our knowledge of the factors that influence electronic and thermochemical properties, spectral features, reactivity etc. as the number of atoms/molecules in the cluster is increased. Illustrative examples have been taken from the research efforts of different groups around the world  $[(Au)_n, SF_6 \cdot (Ar)_n, (Pb)_n, (N_2O)_n, (Xe)_n, (Ar)_n, (Ar)_n \cdot He]$ . The author's group at the Bhabha Atomic Research Centre has investigated IR spectra of clusters using a semiconductor diode laser. The bibliography at the end of the chapter is extensive.

For a long time, chemists have postulated that 'reactants' pass through a 'transition state' on their way to 'products'. The question of characterizing the transition state (TS) has engaged the attention of theoreticians and experimentalists. The chapter 'Probing the transition state' (N. Sathyamurthy) and a section of the chapter 'Photodissociation dynamics' (P. K. Das) address this problem. The definition of TS has undergone a change in the sense that there is no unique TS but an intermediate region with many possible configurations that are collectively called the 'transition state'. It is now possible to probe the TS directly, and the classical experiments of Polanyi in monitoring the 'wings' of the sodium D-line emission in the reaction  $F + Na$  are illustrative. Other similar findings by frequency-domain studies of photodissociation of  $O_3$ ,  $CH_3I$ ,  $NO_2$  and  $H_2S$  have been described. Perhaps a more convincing method of probing the TS is direct observation of the evolution of the TS from a zero time when the reaction is initiated and of its subsequent progress to the product state. Experiments in the picosecond and, more dramatically, in the femtosecond time domain have demonstrated our ability to 'observe' in real time the reacting molecule pass through the TS to the product state. The TS in the photodissociation of  $ICN$ ,  $NaI$  and  $I_2$  is amenable to observation by femtosecond transition-state spectroscopy. The IIT Kanpur group has done theoretical studies on the spectral manifestation of the TS in the  $(H, H_2)$  collision.

The so-called half-collision reactions, photodissociations, constitute a major area of research, following the availability of a variety of lasers with wide-ranging specifications. In the first half of the eighties state-to-state studies were the dominant ones. The photodissociation studies discussed in this book concentrate on major recent studies on vector correlations in state-to-state photodissociations, external control in unimolecular-dissociation product yields, and photodissociation of adsorbed species on solid surfaces—these studies have become feasible on account of the availability of femtosecond lasers, narrow-band tunable lasers, highly sensitive detectors, efficient pumps, etc. With OCS as the chosen example, it is shown how vector-vector correlation studies can yield a detailed picture of the mode of dissociation. The method of coherent radiative control of the path of a unimolecular reaction (when more than one product exit channel are available) is discussed theoretically—no experiments have yet been performed. The characterization of catalysed reactions of short-lived radicals on metal, semiconductor and insulator surfaces has been rendered possible by laser-induced processes on surfaces. Typically an adsorbate, such as  $CH_3Br$ , adsorbed on an ultraclean, chosen face of a single crystal (preferably in a monolayer) is subjected to a polarized or unpolarized beam at a known incident angle. In this case  $\cdot CH_3$  is released from the surface, and one can attempt to answer several questions about the dissociation dynamics: (i) Is the photodissociation totally non-thermal? (ii) Is it a surface or bulk effect? (iii) Are there preferred geometries and preferred sites? (iv) Are the molecules in the adsorbed state when the rupture takes place? In addition, if the species formed is not immediately released will it partake in further reactions at the surface? An extensive bibliography on the subjects discussed is included.

The scattering of beams of molecules and atoms from a surface is a very powerful method for the study of the interactions of atoms and molecules with that surface. While only a few experiments of this nature are available, considerable development has taken place on the theoretical front. In

'Dynamics of gas-surface scattering' K. L. Sebastian discusses both elastic and inelastic scattering. In the inelastic case, besides the rotational, vibrational and electronic excitation of the gas molecule, phonon and electron excitation of the surface can occur. The theoretically predicted signatures for such excitations have been compared with the features observed in the experimental scattering data.

Surface phenomena can also be selectively studied by taking advantage of the fact that second-harmonic generation is possible only at the surface and is forbidden in the bulk of a liquid (K. Bhattacharyya). What is typically measured is the intensity, the phase and the polarization of the second harmonic generated by the adsorbed species at the surface. While polarization depends on the relative orientation of the adsorbed species at the interface, the phase gives the absolute orientation, and the intensity is related to the interfacial populations. Using this technique it has been possible (i) to investigate chemistry at interfaces, using steady-state and time-resolved techniques; (ii) to study biological membranes, which are essentially oriented dipole layers and hence capable of efficient harmonic generation; and (iii) to study the changes that occur in the molecule on adsorption on a surface.

Reaction dynamics in the liquid state has been considered by two authors. One considers the dynamics of barrier-

less reactions (B. Bagchi) such as fast photoisomerization or photo-induced electron transfer. The author presents a molecular theory—in whose development he has played a major role—that takes into account the effects of collective solvent dynamics and predicts that, in barrierless (or very-low-barrier) electron-transfer reactions in dipolar solvents, the rate of electron transfer is critically dependent on solvent motion, especially translational motion. For photoisomerization reactions, the reaction motion is a rotational diffusion on a potential surface. The second author considers electron transfer in polar liquids (B. L. Tembe) where a barrier is present and the transfer is thermally activated. He has presented his theoretical model, which accounts successfully for the aqueous ferrous-ferric electron-exchange reaction. The treatment employs classical statistical mechanics, and the contribution from solvent dynamics is expressed in terms of vibrational or rotational relaxation times calculated by molecular-dynamics simulations.

The time-dependent quantum fluid dynamics formalism has been shown to be applicable to the study of chemical dynamics (S. K. Ghosh). The author, one of those who developed the methodology, has given a good outline of the underlying theory and assumptions. However, the accuracy of the predictions and the efficacy of the method in treating larger systems is not established yet and much remains to be done.

The chapter 'Chaos in chemical dynamics' (R. Ramaswamy) discusses the fundamental notions of chemical chaos and the problem of quantum chaos. The role of chaos in promoting intramolecular energy transfer in irregular scattering in systems where one of the degrees of freedom asymptotically becomes unbound and in non-conservative systems where the total energy is not held constant have been discussed. It is well known that in systems with complex chemical kinetics periodic and aperiodic behaviour are observed and that nonlinearity is ubiquitous in nature.

The authors are relatively young practitioners in the field and it is heartening to see the Indian contributions, especially on the theoretical front. The book draws our attention to the emergence of beautiful experiments that lead us to a more detailed understanding of the various steps involved in a chemical reaction. Even though the coverage and usefulness of certain chapters are inadequate, the book can be strongly recommended for scientists who wish to undertake research in the area of reaction dynamics and to the post-graduate teachers who wish to introduce their students to the fascinating developments in this area. It is a must for all chemistry libraries.

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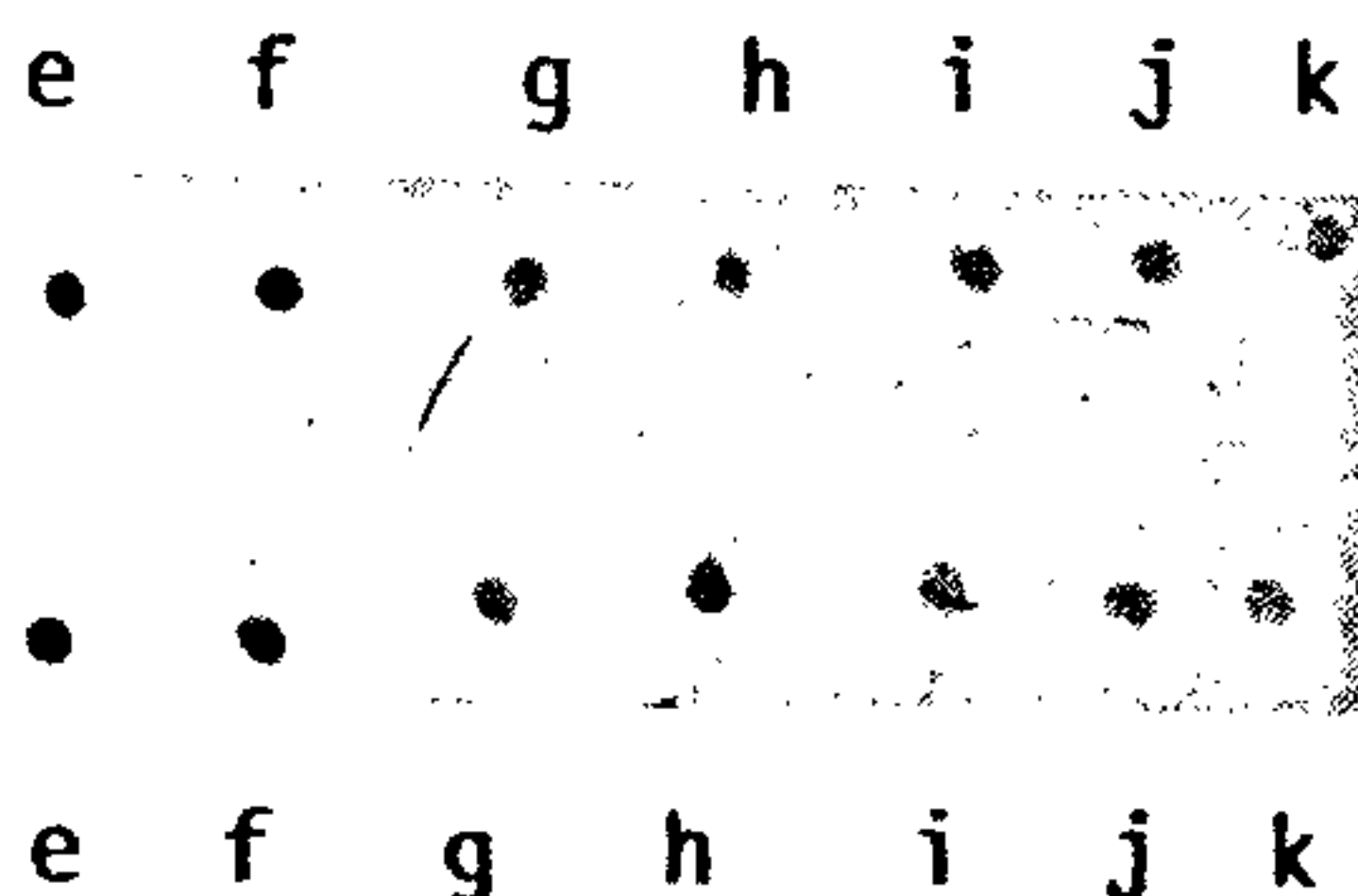
## Erratum

### 5-Methylcytosine residues in DNA decrease during ageing

Deepti D. Deobagkar and Sohan P. Modak

(*Curr. Sci.*, 1991, 61, 483)

The lower panel of Figure 1 on page 484 was printed upside down. The correct figure is given below.



## Correction

### Quaternary tectonic history of northwest Himalaya

K. S. Valdiya

(*Curr. Sci.*, 1991, 61, 664)

Figure 2 on page 665 is slightly modified after Kotlia, B. S. (ref. 21, page, 40, fig. 2) and Figure 3 on page 666 is based on Cromin, V. S. (ref. 3, figs. 1 and 5).