ION-MOLECULE REACTIONS

Precision Kinetics

from our Molecular Physics Correspondent

ONE of the most encouraging things about the present renaissance in chemical kinetics is the steady advance of both theory and experiment along lines which interconnect to a far greater degree than seemed possible ten years ago. While experimentalists are continually refining the accuracy with which the elementary reactive collision can be observed, theoreticians are beginning to grasp the nettle of calculating from quantum-mechanical principles the energy surfaces which must underlie any precise dynamical description of the sequence of events during a bimolecular encounter or a decomposition. One thing is important above all for this programme—the accumulation of reliable and precise data for reactions involving atoms and molecules with as few electrons as possible.

What is perhaps the most precise and thorough study ever made of a bimolecular reaction with small atoms has recently been completed at the Hahn-Meitner Institute in Berlin by Von G. Bosse, A. Ding and A. Hengelein (*Ber. Bunsenges.*, **75**, 413; 1971). The reaction concerned is the ion-molecule process

$$O_2^+ + D_2 \rightarrow O_2D^+ + D$$

The accuracy achieved required a skilful combination of the most refined techniques for beam generation, definition and product detection, which, until recently, were more likely to be reserved for an atomic physics experiment. The O_2^+ ions could be generated in both the $^4\pi_u$ and $^2\pi_g$ electronic states; they were accelerated into a collision chamber containing deuterium, beyond which the scattered reaction products could be analysed for both angular distribution and energy using a quadrupole mass spectrometer with 'Channeltron' detectors. A variety of striking results emerged.

As a preliminary, Bosse *et al.* show that reaction of $^2\pi_g$ O_2^+ sets in at a precise threshold energy (1.7 eV centre of mass) which corresponds closely to the independently calculated endothermicity of the reaction. This explicit demonstration of an activation energy — the fundamental experiment of chemical kinetics, in fact—would have been a sensational result in its own right not many years ago. The principal conclusions, however, are drawn from a series of energy-dependent scattering profiles obtained to quite unprecedented accuracy. Here the crucial feature is the presence or absence of isotropic scattering (centre of mass system) in the reactive-scattered beam of O_2D^+. This is now accepted as a sensitive indicator of the effective lifetime of a collision complex in a bimolecular encounter. Isotropic scattering arises where the lifetime is longer than or comparable with a rotation period; a "forward peak" in the scattering profile indicates a virtually instantaneous "stripping" mechanism for the process. By a peculiar quirk of the present reaction both possibilities can be observed in different energy ranges. With the $^2\pi_g$ O_2^+ ion there is a long-lived complex at low incident energies (17 to 40 eV laboratory system) giving way at higher energies to a stripping mechanism in which the O_2^+ ion seems to extract one deuterium atom with virtually no momentum transfer to the other one. With O_2^+ in the $^4\pi_u$ state, however, there is no sign of a long-lived complex at any energy, a finding almost certainly connected with the strong repulsion caused by the parallel alignment of spins in the recoiling products. Much additional information is also extracted concerning interaction cross-sections, isotope effects with HD rather than D_2, and the role of angular momentum. Significantly, almost all the heat of reaction in the exothermic $^4\pi_u$ reaction finds its way into translational energy of the fragments rather than into rotation.

There will certainly be much food for the theoretician in the results of Hengelein's group and a strong stimulus to the search for other interesting reactions of comparable simplicity. At the same time, in setting new standards for the precision possible in ion-molecule studies, the results confirm that it is likely to be many years before anything like this degree of detail is possible in the results of experiments with neutral beams, notwithstanding the great advances recently made with these.

Although on the theoretical side enormous difficulties remain before a reaction, even of this simplicity, can be treated *ab initio*, there is still a great deal which can be learned by semi-empirical and computer simulation methods. One of the most striking aspects of the present move towards fundamentals is the shift which has occurred over the years in the use of the term mechanism, particularly so far as bimolecular gas reactions are concerned. No longer does this denote simply the gross particulars of intermediate stages which can be written out in chemical formulae; the term has increasingly taken on the meaning of collision mechanism; that is to say, a reference to the subtleties of the collision complex itself, its formation, lifetime and mode of decay, the arrangement of energy in its different degrees of freedom. The elucidation of the

Origin of Cosmic Rays

ALTHOUGH it is almost sixty years since Hess established the existence of cosmic rays the question of what fraction of the radiation, if any, comes from outside the galaxy is still unresolved. The Sun can on occasion produce charged particles with individual energies of up to 10^{10} eV. This energy overlaps the lower end of the cosmic ray energy spectrum in the region where most of the total energy resides, but the total output of this form of solar energy is very low and even if all other stars were as productive the observed cosmic ray energy density cannot be accounted for in this way. Because of this it is current fashion to think in terms of super novae explosions or pulsars as the principal generators of cosmic rays.

At the other end of the spectrum cosmic ray energies seem to go as high as 10^{19} to 10^{20} eV, if the interpretation of the large air showers is to be believed, and it has been customary to invoke an extra-galactic source for these super high energy particles because of the difficulty in finding sources with sufficiently high magnetic fields to accelerate them and because the interstellar magnetic fields are too weak to contain them within the galaxy.

Up to a few months ago the available picture of the general shape of the cosmic ray energy spectrum lent credence to a mixed galactic/metagalactic origin for the particles, but recent analyses of data from the large air shower array at Haverah Park have shown that the apparent decrease in slope of the spectrum above $\sim 10^{17}$ eV which was observed in earlier work at Volcano Ranch is almost certainly illusory. This change in slope had been attributed to a metagalactic cosmic ray flux.

In next Monday's *Nature Physical Science* F. W. Stecker re-examines the question of cosmic ray origin in the light of these results and of the interaction that should take place between ultra high energy metagalactic cosmic rays and the photons of the 2.7 K black-body radiation field. This interaction should lead to an upper energy limit to the cosmic ray spectrum and to a universal gamma-ray flux. Stecker considers several alternative cosmic ray models and concludes that the new spectral shape and the established upper limit to the gamma-ray flux are best explained in terms of a purely galactic origin for cosmic rays of even the highest energy. He offers only two alternatives; either the energy of air showers with $E \gtrsim 6 \times 10^{19}$ eV has been overestimated or there is no universal black-body radiation.