Pimentel’s Matrix

George Claude Pimentel
(1922-1989)

Middle age can be tough. Year ago, I remember a seminar given by Martyn Poliakoff about the photolysis of transition metal carbonyls at low temperature. As he spoke of delicate noble gas complexes, a chemist in his 50’s, who was clearly drunk, heckled Poliakoff, bellowing in broad Yorkshire tones that “It’s not real. You can’t put that in a bottle”. The bizarre incident highlighted for me the way in which, through the 20th century, chemistry moved from the study of the ground state – starting materials and products – to the isolation and study of the fleeting intermediates and excited states that were being invoked to explain chemical reactions.

The period after the first world war saw the development of a raft of chemical techniques through the development of pumps, valves, cryogenics and, of course spectroscopy. Thus by early in the 1940s the existence of unstable molecules like imine had been conclusively established by detailed spectra in the gas phase that confirmed many of the prediction of the new molecular orbital theory. At Imperial College, a young chemist, Kenneth Stewart working with the inspirational inorganic chemist Harry Emeléus, generated imine in the gas phase and began to explore its chemical reactivity. He condensed it onto liquid air-cooled traps, noting a blue colour that disappeared on warming; when co-condensed with benzene it generated aniline. The work ended when Stewart abandoned chemistry to enlist in the armed forces in 1940 – he would later become a leading nuclear weapons expert at the British Atomic Weapons establishment at Aldermaston. But he had planted key intellectual seed.

At the same time the American chemist Gilbert Lewis was exploring a curious phenomenon that had been observed since the 1890’s in Germany: that dyes like fluorescein dissolved in frozen organic solvents or boric acid (a material notorious for forming glasses rather than crystallizing) would phosphoresce for long periods. Lewis, wanting to understand the photophysics began measuring their spectra and decay rates. Crucially, Lewis and his students developed a solvent mixture, that they called EPA consisting of ether, isopentane and alcohol, that gave a consistently clear glass ideal for both photolysis and spectroscopy. With it, Lewis and his student David Lipkin reported a detailed study of tetraphenylhydrazine and related molecules in which the ultraviolet light was used to generate $Ph_2N^{\cdot}$ radicals that could be observed for many hours when frozen in EPA.

The use of EPA as a medium for conducting low temperature photochemistry spread quickly. At Berkeley, the photochemist George Gibson (who had been PhD supervisor to Henry Eyring and to the Nobel Prize winners William Giauque and Glenn Seaborg) used the glass to study the photolysis of benzene at low temperature.

The work was also noticed by one of colleagues, George Pimentel, a young and ambitious chemist who was specializing in the study of hydrogen bonding and structures of unusual molecules by infrared spectroscopy. Born in California, his father was a builder who had barely finished third grade while his mother’s education had gone only part way through secondary school. But as a teenager Pimentel could cycle to Caltech where Robert Millikan gave public lectures, and he was soon hooked into science.

He studied chemistry at UCLA. When he graduated in 1943 he was seconded to Berkeley to the Manhattan project where he worked on isotope separation with Wendell Latimer, a former student of George Gibson’s. When the war ended he started a PhD at Berkeley with one of Latimer’s students, Kenneth Pitzer, one of the pioneers of infrared spectroscopy. Pimentel hoped to extend the use of IR to the study of unstable radicals and as Pimentel and his British postdoc Eric Whittle pondered the project they came across a detailed vibrational study of ammonium halides by Donald Hornig at Brown University.

Hornig had constructed a copper frame into which a flat slab of rocksalt could be mounted (see diagram). The frame incorporated a thermally conductive copper block attached to a glass reservoir that could be filled with a cryogenic liquid to cool it to low temperatures. The entire assembly sat inside a vacuum jacket, so materials could be sublimed onto the window and studied spectroscopically

Pimentel, Whittle, and graduate student David Dows decided to try to catch the free radicals, including imine, formed in the decomposition of hydrazoic acid, HN_3, using Hornig’s apparatus. But then Pimentel had an idea – why not use frozen but infrared-transparent noble gases to delicately cradle the trapped radicals? After months of failure to get the conditions just right, Dows and Whittle demonstrated proof of principle by trapping $NO_2^{\cdot}$ radicals using frozen CO_2; then they moved to lower temperatures. With William Giauque’s low temperature thermodynamics lab nearby, supplies of liquid helium and hydrogen were plentiful. With its bigger heat capacity, hydrogen was a much more effective, if dangerous, coolant. Pimentel called their new technique “matrix isolation”.

But a mere four days after the Pimentel’s paper was submitted in 1954, George Porter in Cambridge reported a very similar idea. Porter, who had developed the flash photolysis technique to study fast reactions in the gas phase, imagined being able to trap the intermediates using hydrocarbon or EPA glass. He and his American research fellow, Irwin Norman, designed Dewar flasks incorporating optically flat quartz windows. A solution of iodine in EPA, frozen onto the window, bleached beautifully on ultraviolet irradiation; the colour returned on warming suggesting the splitting and recombination of the iodine molecules. Studies of many organic molecules would follow.

But Pimentel’s colder, vibrational approach that was the more structurally revealing, and caught on rapidly, especially as the group improved and optimized the apparatus to operate at the lowest temperatures. The spectral lines were sharp and the availability of isotopes made assignment straightforward.

Prof Jim Turner, a Pimentel postdoc in the early 60’s, remembers the entire department being assembled at short notice for the electrifying announcement that Neil Bartlett had isolated compounds of xenon. Turner, who was in possession of Berkeley’s only cylinder of xenon, conducted experiments with fluorine in cold matrices of the element. Pimentel’s infectious enthusiasm – “Let’s try it” was his catchphrase – and his clarity of thought are beautifully captured in a short film that was made at the time (https://archive.org/details/research_problem_inert_gas_compounds) for Pimentel’s national CHEM Study education project that included an ambitious and influential textbook, Understanding Chemistry, that was widely translated. The textbook was also memorable, however, for including a statement that rare earth chemists have never quite been able to forgive: “Lanthanum has only one important oxidation state in aqueous solution’ the +3 state. With few exceptions that is the whole boring story of the other fourteen elements”.

But Pimentel was not done with infrared spectroscopy. Using molecules trapped in cryogenic matrices he was able to demonstrate infrared photochemistry, demonstrating for the first time how one could excite molecules to react in a specific way depending excitation mode. At the same time he began to conduct flash photolysis experiments like George Porter’s, but with infrared detection. This required exceptionally fast and sensitive germanium detectors along with cells with very long path lengths to detect radicals like CF_2 and CF_3. By rotating a grating at high speeds it was possible to scan spectra at unprecedented speeds.

It was while using this ultrafast spectrometer in a multi-reflection cell to study the dissociation of CF_3I that Pimentel and his student Kasper observed a huge emission from atomic iodine that swamped their detectors, serendipity giving birth to the chemical laser. Lasers based on the reaction of hydrogen with chlorine and fluorine followed, resulted in an explosion of understanding in chemical dynamics.

In 1969 Pimentel, then Chairman of the Chemistry Department at Berkeley, applied to NASA to become a scientist-astronaut and was selected as one of the seven finalists. Although he never travelled into space, he proposed developing an infrared spectrometer for the Mariner 6 and 7 spacecraft to look for signs of life on Mars. The weight and power requirements were almost unimaginable. But the instrument worked beautifully and provided the first detailed look not only at the composition of the atmosphere but also of the ice caps, and surface minerals. And by looking at the intensity of the CO_2 bands as the probes orbited the planet, the spectrometers also provided some of the earliest maps of the topography of the red planet.

Matrix isolation provided the “bottles” to contain and study seemingly impossible species. That we are almost blasé about such studies today, speaks to the success of Pimentel, Porter and the others who made it all possible. And before you feel too smug about Poliakoff’s heckler, if you’re not in the first bloom of youth, I bet there’s some technique around today that makes you feel uncomfortable too.

References

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