Thomas Midgley

Topics

Periodicity, environmental chemistry, chemists

The story of Thomas Midgley is something of a classic in terms of chemistry teaching anecdotes. Midgley was an engineer by training but used a knowledge of chemistry and, in particular, the Periodic Table to make two significant developments – lead-based anti-knock additives for internal combustion engines and chlorofluorocarbons (CFCs) as the working fluids in refrigerators. Both these developments were of enormous commercial importance at the time (the 1920s) and remained in use for over half a century.

Unfortunately, both have led to significant environmental problems which have resulted in their being phased out in recent years. This, too, can generate important teaching points.

The Midgley story also has 'anecdotes within anecdotes' – the stories of how he dealt with the embarrassment of the powerful garlic body odour caused by tellurium poisoning during his research into anti-knock additives and the spectacular way in which he demonstrated to the American Chemical Society that CFCs were non-toxic and non-flammable by inhaling the gas and placing a lighted candle in his mouth.

Finally, and with nothing to do with chemistry, there is the tale of Midgley's tragic and bizarre end. At the age of 51, Midgley contracted polio and lost the use of his legs. Using his engineering skills he devised a pulley system to enable him to get out of bed. This worked well until one day he became entangled in the ropes and was strangled.

Lead-based fuel additives

Thomas Midgley was born in 1889 in Pennsylvania, USA, and took a PhD in engineering at Cornell University. In 1916 he was working for a company called Kettering that made small electrical generators for use on farms. These generators ran on kerosene (paraffin) and often ran into a problem called 'knocking 'in which the fuel ignited too early (as the piston was rising up the cylinder rather than when it was at the top). This caused rough running and inefficiency.

Midgley developed a theory, based on some rather dubious physics, that dyeing the fuel red might help reduce knocking. The first substance readily available to him that would do this was iodine and, sure enough, adding iodine to the paraffin did reduce knocking. However other red dyes had no effect, but he did find that adding iodoethane (ethyl iodide) also had an anti-knock effect – suggesting that the element iodine was a key factor. At this point, Midgley began to use the Periodic Table to systematise his search.

> 'In the course of my education I had occasion to learn about the Periodic Table and to have it impressed on my memory as a very useful tool in research work … we abandoned the method of trial and error in favour of a procedure based on the Periodic Table. Predictions began fulfilling themselves instead of fizzling out …'

In general, anti-knock effect increased on descending a Group and increased on moving from right to left across a Period. Interestingly, the effect seemed to be associated with elements (alone or combined), rather than specific compounds. The compounds had, of course, to be soluble in paraffin and a number of them were organo-metallic.

Following these trends, one of the compounds investigated and found to be effective was diethyltelluride. This led to the story about tellurium poisoning. Even minute amounts of tellurium or its compounds inhaled or absorbed through the skin give rise to this. The characteristic sign of this is a sour garlic-like odour on the breath and in body excretions such as sweat. (The resemblance of the odour to that of garlic may not be a coincidence because the garlic plant contains relatively large amounts of tellurium, and it has been suggested that the characteristic odour of garlic may be caused by volatile tellurium compounds.) Midgley's work involved a good deal of travel by train and the body odour was potentially embarrassing. One account relates how Midgely would ' .... go into a smoking car and sit down beside the swarthiest individual in the car in hope that the other passengers would blame the hapless individual for the odour which soon pervaded the car.'.

Eventually tetraethyllead(IV) became the anti-knock additive of choice and was used in petrol until it began to be phased out in the 1970s and was totally withdrawn in the UK in 2000. This was because lead compounds are poisonous, and studies suggested that the lead(IV) oxide given out by vehicles using leaded fuel was causing brain damage in children growing up in areas close to major roads. Lead also poisons the catalysts of cars using catalytic converters used to convert carbon monoxide, nitrogen oxides and unburned hydrocarbons in car exhausts into innocuous carbon dioxide, nitrogen and water. (NB There is more information on pollution by lead from motor exhausts in D Warren, *Green Chemistry*, London: Royal Society of Chemistry, 2001)

CFCs

Refrigerators work using a volatile liquid called the refrigerant kept in a sealed system of pipes. Outside the fridge the liquid is compressed by a pump. It then passes into the ice box and is allowed to evaporate to become a gas. Evaporation absorbs heat and this cools the fridge. The gas then passes out of the fridge to be compressed back to the liquid state – a process that gives out heat (this can be felt in the pipes behind the fridge). The refrigerant therefore has to be suitably volatile, *ie* have a boiling point within a fairly narrow range of temperatures. In the 1920s, compounds such as propane, ammonia, sulfur dioxide and chloromethane were used. All had disadvantages such as toxicity, flammability or chemical reactivity. What was required was a non-toxic, non-flammable, chemically inert gas/volatile liquid. In 1928, Midgley was called in to help the search.

Essentially what he did was a database search but, having used the Periodic Table so successfully in his search for anti-knock additives, he used it again to inform his search. In general, metal compounds are involatile (because they are ionic) so he concentrated the search on compounds of the non-metals at the upper right hand side of the Periodic Table (excluding Group 0, as these are all gases) plus hydrogen. These were: carbon, nitrogen, oxygen, fluorine, sulfur, chlorine, bromine and hydrogen.

Midgley and his colleagues noticed two things. First, flammability decreases from left to right in the Periodic table for compounds of these eight elements. Second, toxicity generally decreases from the elements at the bottom to the elements at the top. This led to the suggestion that fluorinated compounds might be worth considering. Eventually chlorofluorocarbon compounds (CFCs) were chosen. One of the first of these to be used was dichlorodifluoromethane (CCl_2F_2) later given the trade name Freon. It had a suitable boiling point, was chemically stable, non-toxic and non-flammable. With a degree of showmanship, Midgley demonstrated these properties at a meeting of the American Chemical Society by inhaling some of the gas and then exhaling onto a lighted candle, which was extinguished.

Freon and other related CFCs went on to be an important commercial success, being used for several decades as refrigerator fluids and for many other uses such as ‘blowing’ insulating foams. We now know that the chemical inertness of the CFCs (due in part to their strong C-F bonds) held the seed of a major environmental problem. On release into the atmosphere, CFCs do not break down and a large ‘reservoir’ of them built up in the atmosphere. However, high in the atmosphere they *do* decompose under the action of ultraviolet light, leading to the formation of chlorine radicals which catalyse the breakdown of ozone to oxygen. Since ozone absorbs ultraviolet radiation from the Sun, this leads to a greater intensity of UV radiation at the Earth’s surface causing problems such as increased rates of skin cancer, cataracts in the eyes, the death of plankton and faster decomposition of rubber, plastics and dyes. This began to be understood in the 1970s and CFCs have been withdrawn since the Montreal Protocol of 1987.

The chemistry of the ozone breakdown is as follows.

High in the atmosphere are found oxygen molecules, ozone, oxygen atoms and chlorine radicals. The last two are formed by the decomposition of CFCs and oxygen molecules respectively under the action of ultraviolet radiation from the Sun. The following reactions then occur.

$Cl^{\cdot} + O_3 \rightarrow ClO. + O_2$

$ClO^{\cdot} + O \rightarrow O_2 + Cl^{\cdot}$

Overall the reaction is

$O_3 + O \rightarrow 2O_2$

The $Cl^{\cdot}$ is regenerated and can go on to be involved in further reaction steps so that a single chlorine radical can cause the breakdown of many ozone molecules.

Afterword

It is easy to deride Midgley as being responsible for two environmental catastrophes. This is, of course, with hindsight. At the time both tetraethyllead and CFCs were major scientific and economic breakthroughs and their consequences a half a century later simply could not have been predicted by Midgley or anyone else – they were truly ‘chemicals for their time’.