

Re: Chemical synthesis of F2

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"Rue John D'Ian" <istjohn@xxxxxxxxxxx> A lifelong pursuit of "impossible" chemistry. Christe, Karl. Loker | Hydrocarbon Research Institute, University of Southern California, Edwards |

[snip]

New Scientist 6 May 2000
Opinion interview

Handle with care!

Karl Christe takes danger in his stride. He has to. In forty years as a chemist developing explosives and rocket propellants, he's seen how bad it can get. But then, it's not an area that attracts faint hearts. Christe has earned a reputation for ignoring conventional wisdom. He's synthesised dozens of previously unknown compounds several the test books said were impossible. His latest made headlines last year as one of the most violently explosive materials ever produced. It was also the first new form of nitrogen in more than a century. Jonathan Knight wondered what spurred him on ...

You spent many years developing rocket fuel for the civil sector, now you're doing more explosive work for the US Air Force. How come?

I came to the US after getting my PhD in Germany and worked as a fluorine chemist for five years in the Bay area. Then a colleague has an accident that burned down the laboratory. That and a shift in commercial interests prompted the company to cancel its fluorine research. The leader in rocket propulsion was Rocketdyne. I convinced them to hire me and worked there for 27 years making novel rocket fuels and oxidizers. That also came to an abrupt end when two colleagues got killed. They were burning old explosives and had a premature ignition. Rocketdyne abandoned chemistry. I wanted to continue, and the USAF research laboratory in Edwards was one of the few places where basic rocket propulsion research was still being done.

Do such accidents happen often?

No, they're very rare. These were people working on conventional explosives on a large scale. Usually it's human error or poor judgement. It's no more dangerous than

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mining or the chemical industry.

So you've really got to know what's worth trying and what isn't?

You must use your own judgement to decide if a compound should exist or shouldn't exist. If conventional wisdom says something can't be made, the challenge is to make it anyway. The reason I have tried so many different things over the years is I get very bored with routine work. I want to do the breakthrough work on energetic materials and let other people fill in the details.

Is the term "energetic materials" a euphemism for explosives, or is there a difference?

No, it doesn't mean exclusively explosives. There are different applications for energetic materials—they can be used as rocket propellants, or in batteries or fuel cells.

So not all energetic materials would work well as explosives?

Absolutely. You need a certain detonation velocity. If something just burns and it releases a lot of energy but the kinetics are too slow, then it wouldn't make a good explosive. You have to know what the kinetics are, whether it decomposes very rapidly or not. If you have a reaction going in a closed container, you build up pressure, and the reaction kinetics increase with the square of the pressure. So in a closed container, what starts out as combustion will turn into an explosion. But if you have the same material in a wide open system, burning won't turn into an explosion—you'd get propulsion.

One of your early successes was to make elemental fluorine using a chemical reaction even though everyone said it could only be done electrochemically. How did you do it?

In 1986, I was invited to give a review paper on the chemical synthesis of fluorine at a jubilee celebrating the discovery of fluorine. As I started to make my visuals, I realized it would make a hell of a boring lecture to tell everyone you can't make it. You could read that in any high-school textbook. I became convinced that there was no reason why you shouldn't be able to make it. So a week before the meeting, I went into the lab, and in three days I had made elemental fluorine by chemical means.

Last year, you made the N₅⁺ ion, the first new form of nitrogen in more than 100 years. Didn't you blow up a piece of equipment in the process?

Well, you know that sort of thing is usually blown out of proportion by the press. All they look for are sensational stories. With N₅⁺ there were press reports that it was the most powerful explosive ever made, but this was hype. For one thing, we can only prepare it as a relatively stable salt. And for another, what does "most powerful explosive" mean? Highest detonation pressure? Highest detonation velocity? Do you include only practical explosives or extremely unstable ones too? It's not black and white.

So what really happened?

Our experiment was carried out on a very small scale, and maybe 2 or 3 milligrams of the material shattered a glass flask. It was quite spectacular that such a small amount could do so much damage. Our first expectations were that the compound would be

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very unstable and very violent when it decomposed. But since we had been able to handle it safely up to that point, I was very concerned that maybe we hadn't made it after all.

So you were relieved when it blew up?

Yes.

Are you still working with nitrogen?

Yes, we're trying to make the first allotrope of nitrogen, which is an extension of the N_5^+ work. An allotrope is an alternate molecular form of an element. With carbon you have diamond, graphite, buckyballs. Sulphur has almost 30 allotropes. But nitrogen has none, there is only nitrogen gas, N_2 . By itself, N_5^+ isn't a nitrogen allotrope because it's charged. But if you can make a counter-ion exclusively of nitrogen, you'd have a true nitrogen allotrope. So we want to make $N_5^+N_3^-$. This is much more challenging than making other allotropes because nitrogen allotropes are extremely unstable and explosive. It's like a ball sitting on a very high mountain with just a tiny ledge keeping it from rolling downhill.

So this allotrope is even more dangerous than the N_5^+ salts that you already made?

Imagine surrounding each energetic N_5^+ ion with a sort of padding, much as you would protect a box filled with very fragile glass bulbs. If there is packaging material—ions—between each bulb, the implosion of one bulb won't spread. Now take the packaging material out, and put explosive material in between the bulbs. If one bulb goes, the whole box immediately blows up. That's the difference between N_5^+ and its "packaging" ions and something like $N_5^+N_3^-$ where the balancing anion is also energetic. You're walking a very fine line.

Wouldn't N_6 be neutral by itself? Why not make that?

Cyclic N_6 , the benzene analogue, is unstable. Catenated N_6 which has a Z shape, should be more stable. It might be possible to make it by combining two N_3 radicals. The problem with catenated N_6 , however, is that its central bond is quite weak and its barrier to decomposition is low. I work with numerous theoreticians on this. I come up with a structure that looks desirable to me, they do their calculations if they find one bond is very long know it's a very weak bond and I won't try to make the compound. Remember the ball sitting on top of the mountain. ledge?which represents the barrier to decomposition?is extremely small, then the thermal energy at room temperature will be enough to vibrate the molecule apart. In other words, our ball over at the slightest tremor.

What are these polynitrogen compounds good for?

If we can make $N_5^+N_3^-$, it would be an extremely powerful explosive with a detonation pressure three to four times the state of the art explosives such as HMX and RDX. These are maybe 60 per cent more explosive than TNT. And as a rocket propellant it would double the power of the typical monopropellants that are used today. The question is how sensitive these materials are, because they release so much energy. If they are very sensitive, they could be extremely dangerous. If you have an astronaut

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sitting on top of a rocket, the propellant has to be safe.

Is there a Holy Grail in your field?

Probably a compound that is several times more powerful than the best-known materials, but is completely safe to handle, cheap and environmentally friendly. Polynitrogen wouldn't be cheap and probably not completely safe to handle.

Do you ever worry about the morality of developing these explosive materials?

There's nothing immoral about increasing the energy content of materials. Take nuclear research. You can run nuclear power plants for peaceful applications, or you can build an atomic bomb. The morality of the user is what counts. It's the same thing here. A strong defense is the best guarantee of peace. Just because N₂ is highly energetic doesn't mean we must use it for aggression. We're trying to push the limits of science: we want to make the first allotrope of nitrogen, we want to see how much energy you can pack into a compound and still be able to handle it. You can kill plenty of people with conventional explosives. You don't need any exotic materials.

Joseph Rotblat, the Nobel prizewinner who campaigned against nuclear weapons, suggested that scientists take a Hippocratic oath....

I don't think it's a good idea. How could Albert Einstein or Otto Hahn have predicted that people would build an atomic bomb? To tell them that they should never have done their work because it would find applications in mass destruction would be fatal for science.

Has anything that came out of your work been used in conflicts such as the Gulf War or the NATO action in Kosovo?

No.

Nothing. Not a squeak.

Does your research have any specific peacetime applications?

Yes. We have a contract with a German company to develop industrial materials.

Do you find working with energetic materials stressful?

Doing challenging chemistry in this field is like mountain climbing. It would be suicidal for a recreational hiker to attempt to climb Mount Everest alone without oxygen. But there might be a few highly skilled experts who are willing to test the limits. If they do it right, they have a good chance of succeeding and surviving. We work very carefully on very small scales, so even if something explodes it's more like a firecracker. And we use safety gear.

Have you ever thought, this work is too dangerous, I'm going to pack it in?

No. You have to know what you're working with. It's like driving a fast car. It doesn't mean you shouldn't drive the car, it's just if you do you have to be more careful.

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For a pic of Karl Christe <http://itss.raytheon.com/whats-new/98archive/hedm.html>

donald j haarmann

What we could do with round here is a good war.
What else can you expect with peace running wild
all over the place? You know what the trouble with
peace is? No organization. Bertolt Brecht

• **References:**

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 ◇ From: Wilco Oelen
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